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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]


## THE EFFECT OF CHANGE OF MEDIUM UPON THE VELOCITY OF HYDROLYSIS OF ETHYL ORTHOFORMATE[1]


BY HERBERT S. HARNED AND NICHOLAS N. T. SAMARAS



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The data on the influences of changes of media upon reaction velocities in homogeneous catalysis are fragmentary and to a large extent unreliable. As part of a general investigation of this subject, a careful study has been made of the velocity constant of hydrolysis of ethyl orthoformate catalyzed by acetic acid–sodium acetate buffers both in aqueous solution and in water–organic solvent mixtures. The hydrolysis of this reaction which may be represented by

$$HC(OC_2H_5)_3 + H_2O \longrightarrow HCOOC_2H_5 + 2C_2H_5OH$$

was first studied quantitatively by Skrabal.[2] It is extremely sensitive to hydrogen ions and is therefore completed before any hydrolysis of ethyl formate is detectable. During the reaction no acid is formed and consequently this hydrolysis is admirably suited for the study of hydrogen-ion catalysis, particularly since hydroxyl ions produce no effect. Brönsted and Wynne-Jones[3] showed that undissociated acid molecules show no detectable effect and that the hydronium ion is the effective catalyst.

### Experimental Procedure

**Materials.**—All organic substances employed were the purest obtainable commercially. The ethyl orthoformate was procured from Kahlbaum and Schering and Kahlbaum, both samples yielding identical results. The glycine was a recrystallized sample of a highly pure product. The acetic acid and sodium acetate in the buffer mixtures were of the best grade of analyzed specimens. Small acid or basic impurities were compensated by the buffer, so that the concentration of the only active catalyst, the hydronium ion, was accurately controlled.

**Apparatus.**—The hydrolysis of ethyl orthoformate is accompanied by a considerable change of volume. The expansion of 100 cc. of a 0.05 *M* solution during the

[1] This paper contains part of a dissertation presented by Nicholas N. T. Samaras to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Skrabal, *Z. Elektrochem.*, **33**, 322 (1927).

[3] Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

course of the reaction is about 40 cu. mm., so that the reaction velocity may be studied by the dilatometric method.

The dilatometer employed differed from that employed by Åkerlöf[4] in not having a water jacket around the capillary. The capacity of the reaction vessel was about 125 cc. and the inner diameter of the capillary 0.7 mm.

With certain variations, the technique of operation was the same as described by Åkerlöf. Great care had to be exercised in filling the tubes, which in this case was accomplished more conveniently by pressure than by suction. Because of the sensitivity of the reaction, considerable precaution and acquired skill were necessary to attain the reported accuracy. The accuracy of determination of the velocity constant is estimated to be within $\pm 3\%$ in all cases, some of the series of results being considerably more accurate. The greatest difficulty in the dilatometric method is encountered when employing solvents more volatile than water.

**Method of Calculation of Velocity Constants.**—The reaction is of the first order and, consequently, the velocity constant, $\bar{k}$, may be computed by the equation

$$\bar{k}t = \log (v_\infty - v_0) - \log (v_\infty - v_t) \qquad (1)$$

where $v_\infty$, $v_0$, $v_t$ are the dilatometric readings corresponding to the final state, initial state and the state at the time $t$. All experimental values of $\bar{k}$ will be given in common logarithms, according to equation (1), $t$ being expressed in minutes. Owing to the uncertainty in the initial reading, $\bar{k}$ was determined by plotting $\log (v_\infty - v_t)$ against $t$; obviously, the negative of the slope is $\bar{k}$. All points were consistent and fell on a straight line with the possible exception of the first and second. This was caused by the fact that the solutions in passing over from the mixing flasks, which were immersed in the thermostat, to the reaction tubes were slightly cooled or heated due to small differences between the room temperature and that of the thermostat. Having chosen the value of $v_0$, this graphical method was occasionally checked by an arithmetical calculation. The agreement was quite satisfactory.

## Experimental Results

The catalytic coefficient of the hydronium ion was first determined at 20 and 25°. This measurement was carried out in order to check the value at 20° obtained by Brönsted and Wynne-Jones, who employed cacodylic acid–sodium cacodylate buffers as a source of hydronium ions. The velocity constant at both 20 and 25° was determined in a carefully prepared buffer solution containing 0.005 $N$ acetic acid and 0.05 $N$ sodium acetate. The velocity constant at 20°, $\bar{k}_{20}$, was found to be 0.0401, and at 25°, $\bar{k}_{25}$, 0.0641, respectively. These values represent the means of three experiments at each temperature. The temperature coefficient, $\bar{k}_{25}/\bar{k}_{20}$, equals 1.60.

To determine the catalytic coefficient it is essential to know the value of $K_c$ of acetic acid at 25°, defined by the thermodynamic equation

$$K = \gamma_A^2 \cdot K_c \qquad (2)$$

[4] Åkerlöf, THIS JOURNAL, **48**, 3046 (1926).

in solutions containing sodium acetate. $K$ is the dissociation constant of acetic acid, and $\gamma_A$, the activity coefficient of the acid, $\sqrt{\gamma_H\gamma_{AC}/\gamma_{HAC}}$. $K_c$ in sodium acetate solutions is not known, so that we were obliged to use the values obtained by Harned and Robinson, and Harned and Owen[5] in sodium chloride solutions. Their results give $1.75 \times 10^{-5}$, and $2.60 \times 10^{-5}$, and $2.87 \times 10^{-5}$ at 0, 0.05, and 0.1 $\mu$, respectively.

Since the oxonium ion is the only active catalyst, the catalytic coefficient, $C^t$, may be readily obtained by dividing the velocity by the hydronium ion concentration. Since at a given ionic strength

$$K_c = \frac{m_{H_3O}\, m_{AC}}{m_{HAC}}, \text{ or } m_{H_3O} = K_c \frac{m_{HAC}}{m_{AC}} \qquad (3)$$

we obtain for the catalytic coefficient at 20°

$$C_{20} = k/m_{H_3O^+} = 1.54 \times 10^4, \text{ and at } 25°$$

$$C_{25} = C_{20} \times \frac{\bar{k}_{25}}{\bar{k}_{20}} = 2.46 \times 10^4$$

From the data of Brönsted and Wynne-Jones, $C_{20}$ was found to be $1.49 \times 10^4$, which we consider a good check since entirely different materials and a different form of dilatometer were employed by those investigators. By using $2.87 \times 10^{-5}$ for $K_c$ at $\mu = 0.1$, the values of $C_{25}$ given in Table I were obtained. Although the mean value at the higher ionic strength is somewhat greater than at 0.05 $\mu$, we do not regard this as significant. The mean value of $C_{25}$ is $2.6 \times 10^4$.

TABLE I

CATALYTIC COEFFICIENT AT 25°

$K_c = 2.60 \times 10^{-5}$ at 0.05 $\mu$, $K_c = 2.87 \times 10^{-5}$ at 0.1 $\mu$

| Buffer | Detns. | $\bar{k}$ | $C_{25} \times 10^{-4}$ |
|---|---|---|---|
| 0.005/0.05 | 3 | 0.0641 | 2.5 |
| .001/0.1 | 2 | .0080 | 2.8 |
| .0111/0.1 | 1 | .0870 | 2.7 |
| .0098/0.1 | 2 | .0744 | 2.6 |
| .01/0.1 | 1 | .0813 | 2.8 |
| | | Mean | 2.6 |

The velocity constants in water and in water–organic solvent mixtures are given in Table II. Those in a given column were obtained by the same buffer mixture. As will be shown, the effect upon $\bar{k}$ of change of medium is independent of small variations of hydronium ion concentration, and, therefore, the same buffer mixture was not employed for all experiments. The hydronium ion concentrations which are of the order of $10^{-6}$ $M$ may always be obtained by dividing $\bar{k}$ by the catalytic coefficient. Column (1) contains the concentration of organic solvent in moles per thousand grams of solution, column (2), the velocity constants, column

[5] Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928); Harned and Owen, *ibid.*, **52**, 5079 (1930).

(3), the values of $\log \bar{k}_0 - \log \bar{k}$, where $\bar{k}_0$ is the velocity in aqueous solution, and $\bar{k}$ is the same in the water–solvent mixtures.

TABLE II

VELOCITY CONSTANTS OF HYDROLYSIS OF ETHYL ORTHOFORMATE IN WATER AND WATER–ORGANIC SOLVENT MIXTURES AT 25°

Catalyst: Acetic Acid–Sodium Acetate Buffers

I. Water–Methyl Alcohol Mixtures

| $c$ | $\bar{k}$ (1) | $\log \bar{k}_0 - \log \bar{k}$ | $c$ | $\bar{k}$ (2) | $\log \bar{k}_0 - \log \bar{k}$ |
|---|---|---|---|---|---|
| 0.0 | 0.0440 | 0.0 | 0.0 | 0.0263 | 0.0 |
| .1 | .0437 | .0030 | .779 | .0240 | .0397 |
| .3 | .0424 | .0161 | 1.51 | .0216 | .0855 |
| .5 | .0413 | .0275 | 2.20 | .0195 | .1299 |
| .7 | .0407 | .0339 | 2.85 | .0183 | .1575 |
| 3.0 | .0300 | .1663 | 3.60 | .0160 | .2158 |

II. Water–Ethyl Alcohol Mixtures

| | | | | | |
|---|---|---|---|---|---|
| 0.0 | 0.0287 | 0.0 | 0.0 | 0.0253 | 0.0 |
| .536 | .0258 | .0463 | 1.05 | .0209 | .0830 |
| 1.05 | .0234 | .0867 | 2.78 | .0144 | .2448 |
| 1.56 | .0208 | .1398 | | | |
| 2.45 | .0177 | .2099 | | | |
| 3.32 | .0142 | .3056 | | | |

III. Water–*n*-Propyl Alcohol Mixtures

| | | |
|---|---|---|
| 0.0 | 0.0263 | 0.0 |
| .421 | .0235 | .0489 |
| 1.20 | .0187 | .1481 |
| 1.27 | .0183 | .1575 |
| 1.91 | .0151 | .2410 |
| 2.25 | .0136 | .2864 |

IV. Water–*n*-Butyl Alcohol Mixtures

| | | |
|---|---|---|
| 0.0 | 0.0410 | 0.0 |
| .342 | .0359 | .0577 |
| .660[a] | .0316 | .1131 |

[a] Limited solubility in water.

V. Water–Isopropyl Alcohol Mixtures

| | | | | | |
|---|---|---|---|---|---|
| 0.0 | 0.0388 | 0.0 | 0.0 | 0.0263 | 0.0 |
| .412 | .0343 | .0535 | 1.18 | .0186 | .1504 |
| .797 | .0308 | .1003 | 1.88 | .0156 | .2268 |
| 1.16 | .0290 | .1264 | 2.20 | .0145 | .2586 |
| 1.50 | .0260 | .1739 | | | |
| 1.78 | .0240 | .2086 | | | |

VI. Water–Acetone Mixtures

| | | |
|---|---|---|
| 0.0 | 0.0253 | 0.0 |
| .430 | .0229 | .0433 |
| .837 | .0212 | .0768 |
| 1.23 | .0185 | .1359 |
| 2.05 | .0153 | .2184 |

TABLE II (*Concluded*)

VII. Water–Glycerin Mixtures

| $c$ | $\bar{k}$ | $\log \bar{k}_0 - \log \bar{k}$ | $c$ | $\bar{k}$ | $\log \bar{k}_0 - \log \bar{k}$ |
|---|---|---|---|---|---|
| 0.0 | 0.0298 | 0.0 | | | |
| .571 | .0292 | .0088 | | | |
| 1.58 | .0268 | .0461 | | | |
| 1.60 | .0268 | .0461 | | | |
| 2.09 | .0267 | .0477 | | | |
| 2.33 | .0260 | .0592 | | | |

VIII. Water–Glycine Mixtures

| | | |
|---|---|---|
| 0.0 | 0.0500 | 0.0 |
| .3 | .0550 | − .0414 |
| .5 | .0571 | − .0577 |
| 1.0 | .0590 | − .0719 |

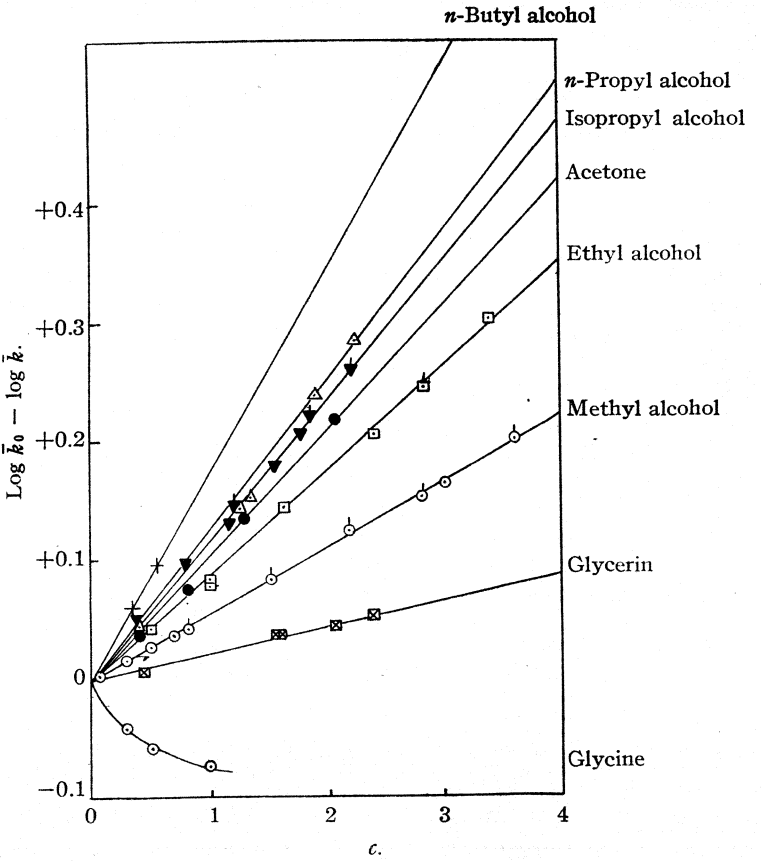


Fig. 1.—Plots of $\log \bar{k}_0 - \log \bar{k}$ against $c$.

## Discussion of Results

In Fig. 1, the values of $\log \bar{k}_0 - \log \bar{k}$ have been plotted against $c$, the concentration in moles of organic solvent per thousand grams of solution. Except in the case of glycine, all these curves are straight lines. Further, the slopes are independent of the strength of the buffer, as shown by the superposition of the plots of the two series of results in the cases of the water–methyl, –ethyl and –isopropyl alcohol mixtures.

Let us now compare those results with the lowering of the dielectric constant of water by the addition of the compounds in question. Unfortunately, with the exception of water–methyl alcohol, water–acetone, water–glycine mixtures, complete data are not available. On the other hand, the dielectric constants of all the pure substances with the exception of glycine are known. The dielectric constants of the water–methyl alcohol, and water–acetone mixtures are given in Table III.[6]

TABLE III

DIELECTRIC CONSTANTS OF SOLVENTS

I. Mixtures

Frequency of applied e. m. f., $4 \times 10^8$

(1) Water–Methyl Alcohol Mixtures, $t = 17°C.$

| Alcohol % by wt. | $D$ | $D_I - D$ |
|---|---|---|
| 0 0 | 82.6 | 0.0 |
| 10 | 77.6 | 5.0 |
| 20 | 72.8 | 9.8 |
| 40 | 63.0 | 19.6 |
| 60 | 52.0 | 30.6 |
| 80 | 42.6 | 40.0 |
| 100 | 33.8 | 48.8 |

(2) Water–Acetone Mixtures, $t = 19°C.$

| Alcohol, % by wt. | $D$ | $D_I - D$ |
|---|---|---|
| 0.0 | 81.8 | 0.0 |
| 25 | 67.7 | 14.1 |
| 50 | 51.2 | 30.6 |
| 80 | 32.2 | 49.6 |
| 100 | 20.7 | 61.1 |

II. Compounds

| Substance | $t$, °C. | $D(\nu = 4 \times 10^8)$ |
|---|---|---|
| Water | 20 | 81.9 |
| Methyl alcohol | 20 | 33.1 |
| Ethyl alcohol | 20 | 22.0 |
| Acetone | 19 | 20.7 |
| Isopropyl alcohol | 20 | 15.7 |
| *n*-Propyl alcohol | 20 | 12.3 |
| *n*-Butyl alcohol | 19 | 7.8 |
| Glycerin | 20 | 16.5<br>43.0 ($\nu = 7.5 \times 10^5$) |

In Fig. 2, $D_I - D$ has been plotted against weight percentage of methyl alcohol and acetone. The results yield straight lines throughout the entire range of concentration. In the absence of any data concerning the dielec-

[6] "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. VI, p. 81.

tric constants of the other mixtures, we shall assume that the same linear relation maintains. In Table III, Part II, are given the values for the dielectric constants of the pure substances from the "International Critical Tables." If the linear relation holds, the curves in Fig. 2 represent the distribution of the results. The plot of $D_I - D$ against weight per cent. of glycine, which is also given, is not a straight line. With the exception of glycerin, the order of the results is the same as that of the $\log \bar{k}_0 - \log \bar{k}$ against $C$ plots in Fig. 1. However, if we use the value for the dielectric constant of glycerin at $\nu = 7.5 \times 10^5$, the result is reasonable.

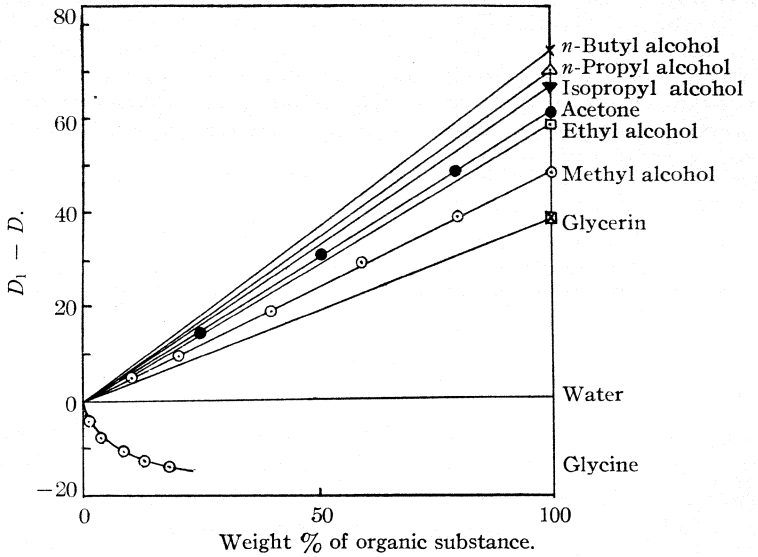


Fig. 2.—Plots of $D_I - D$ against wt. % of organic substance.

From these results, we find that

$$\log \bar{k}_0 - \log \bar{k} = aC \tag{4}$$

and

$$D_I - D = bC \tag{5}$$

which upon combination give

$$\log \bar{k}_0 - \log \bar{k} = \frac{a}{b}(D_I - D) \tag{6}$$

In Table IV are given the experimental slopes, $a$ and $b$, and their ratio.

The constancy of the values in the last column of Table IV shows quite definitely the dependence of the velocity constant upon the dielectric constant. If we plot $(\ln \bar{k}_0 - \ln \bar{k})$ against $(D_I - D)$, a single straight line is obtained, with a slope equal to $2.3 \times 0.032$, or 0.07. Therefore

$$\ln \bar{k}_0 - \ln \bar{k} = 0.07\,(D_I - D) \tag{7}$$

TABLE IV

*a* AND *b* VALUES OF EQUATIONS 4 AND 5

| | *a* | *bb* | *a/b* |
|---|---|---|---|
| Methyl alcohol | 0.0565[a] | 1.564 | 0.036 |
| Ethyl alcohol | .090[a] | 2.759 | .033 |
| Acetone | .105 | 3.553 | .030 |
| Isopropyl alcohol | .118[a] | 3.977 | .030 |
| *n*-Propyl alcohol | .128 | 4.182 | .031 |
| *n*-Butyl alcohol | .171 | 5.491 | .031 |
| | | Average | 0.032 |

[a] Average of two series. [b] The values of $b$ have been computed from $b = (D_W - D_A)/1000 \times W$, where $W$ is the molecular weight of the solvent, and $D_W$ and $D_A$ are the dielectric constants of water and organic solvent, respectively. The dielectric constants are at 20° while the velocity constants were determined at 25°. No temperature correction has been applied since the data are very scarce. This omission will not affect the relative lowering very much; indeed, the correction would not be any greater than the uncertainty of the $D$-values.

Further, the case of water–glycine solutions is interesting. $D_I - D$ for glycine is negative and the plot of $(D_I - D)$ against weight per cent. is of the same form as the corresponding velocity curve in Fig. 1. In addition $(\ln \bar{k}_0 - \ln \bar{k})/(D_I - D)$ is nearly constant but the slope is only 0.015 instead of 0.07.

## Summary

1. The hydrolysis of ethyl orthoformate, a reaction characterized by constancy of the solution acidity, has been investigated experimentally by employing acetic acid–sodium acetate buffers. A dilatometric procedure similar to that described by Åkerlöf has been followed. The catalytic coefficient of the hydronium ion, the only active catalyst in this reaction, has been determined; the result is in good agreement with that obtained by Brönsted and Wynne-Jones, who made use of cacodylic acid–sodium cacodylate buffers.

2. The variations of the velocity constant in water mixtures of methyl, ethyl, *n*-propyl, isopropyl and *n*-butyl alcohols, acetone, glycerin and glycine have been obtained. With the exception of the glycine solutions, all the other series of measurements led to the following single equation for the dependence of the velocity constant lowering upon the dielectric constant lowering

$$\ln \bar{k}_0 - \ln \bar{k} = 0.07\,(D_I - D)$$

In the case of glycine there is an increase in both $\ln \bar{k}$ and $D$, neither, however, varying linearly with the glycine concentration, although $(\ln \bar{k}_0 - \ln \bar{k})/(D_I - D)$ is practically constant and equal to 0.015.

3. A theoretical treatment of those results, as well as other medium changes in homogeneous catalysis, is given in the paper following.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

# MEDIUM CHANGES IN HOMOGENEOUS CATALYSIS AND AN APPROACH TO THEIR THEORETICAL INTERPRETATION

BY HERBERT S. HARNED AND NICHOLAS N. T. SAMARAS[1]

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The velocity of reaction between the substances A, B, etc., may be expressed by the equation

$$v = \bar{k} c_A c_B \ldots . F \qquad (1)$$

in which $F$ is a kinetic factor which is a function of the concentrations $c_A$, $c_B$, etc., of some or all of the species present. $\bar{k}$ is independent of the concentrations, and, consequently, the collision number, is but a function of the temperature.

From the thermodynamic requirements involving the reaction and its reverse, it has been proposed that the kinetic factor must contain the product of the activity coefficients, $\gamma_A$, $\gamma_B$, etc., of A, B, etc., as a consequence of which

$$v = \bar{k}' c_A c_B \ldots . \gamma_A \gamma_B \ldots . F' \qquad (2)$$

This equation will lead to a consistent thermodynamic result when $F'$ is the same for the reaction as for its reverse at the time when the system approaches equilibrium. When $F'$ equals unity, equation (2) expresses the activity rate theory.

A considerable advance in the interpretation of $F$ has been made by Brönsted, who employs the equation[2]

$$v = \bar{k}' c_A c_B \ldots . \frac{\gamma_A \gamma_B}{\gamma_{AB}} \ldots . F'' \qquad (3)$$

where $F''$ is taken to be unity. $\gamma_{AB}$ is the activity coefficient of a hypothetical intermediate complex. This equation has been particularly successful in accounting for positive and negative salt effects in dilute solutions, but does not provide a means of calculating even approximately the actual magnitude of the primary salt effect. In particular this is true in homogeneous catalysis which deals with reactions between ions and neutral molecules.

We shall define "the primary kinetic effect" as the influence of either salt addition or a solvent change upon $F$, and "the secondary kinetic effect" as the change in concentrations, $c_A$, $c_B$, etc., which may occur upon the addition of salts or solvents.

The present treatment of this subject departs somewhat from the point of view just outlined. We shall attempt a calculation of the primary

[1] This communication is a revised presentation of part of a thesis submitted by Nicholas N. T. Samaras to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[2] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1923); *Chem. Reviews*, 5, No. 3 (1928).

and secondary kinetic effects from considerations involving electrostatics, and consider the relations of these deductions to thermodynamics.

**Statistical Theory.**—Christiansen[3] has shown that in cases of reactions between two ions the velocity at constant temperature may be expressed by

$$v = \bar{k}' c_1 c_2 \, e^{-\psi_1 e z_2 / kT} \tag{4}$$

where $c_1$, $c_2$ are the concentrations of the two reacting ionic species, $\psi_1$ is the potential at a distance $r$ from the first ion and $z_2$ is the valence of the second. Upon substituting for $\psi_1$ the value obtained for the potential of an ion from the limiting law of the theory of Debye and Hückel, Christiansen showed that for the case in question Brönsted's equation

$$v = \bar{k}' c_1 c_2 \frac{\gamma_1 \gamma_2}{\gamma_{12}} \tag{5}$$

follows. This equation has therefore a statistical basis and as before mentioned has been proved to be experimentally valid for reactions between ions in dilute solutions.

When, however, we are interested in a reaction involving an ion and a neutral molecule, this equation is not of great help, since in the region of concentration in which it may be expected to be valid, it leads simply to the classic law by reason of the fact that the primary factor, $\gamma_1\gamma_2/\gamma_{12}$, equals unity. Upon extending the theory somewhat, Brönsted showed that a linear salt effect may be expected. No attempt was made by him to compute this effect.

In the present study, we seek the principal cause of the variation of the reaction velocity of reactions between ions and neutral molecules with change in the character of the medium brought about by salt addition or by actual change of solvent. We shall endeavor to show that this change in cases where the catalyst remains the same may be computed by an equation of the form

$$\bar{k} = \bar{k}_0 c \, e^{-W/kT} \tag{7}$$

where $\bar{k}$ is the velocity constant in the medium in question, $\bar{k}_0$ the velocity constant in the original medium before the change was effected, $c$ the concentration of catalyst and $e^{-W/kT}$ a Boltzmann factor. Stated in this manner, our problem resolves itself into ascertaining the character and magnitude of $W$ from fundamental electrostatic considerations. We appreciate that owing to the complexity of the general problem we cannot hope to achieve a complete result, that is to say, to obtain an expression for $W$ which is valid in all cases. On the other hand, we can obtain $W$ for some cases and thereby show that one of the factors of greatest importance is known.

**Electrostatic Theory and the Work Term Involved in Exchange of Solvent and Transfer of Ion.**—The following preliminary treatment

[3] Christiansen, *Z. physik. Chem.*, **113**, 35 (1929).

(equations 8 to 15) is that employed by Butler[4] in a contribution to the theory of the salting out effect, and is presented here in order to make clear the definitions of the quantities involved. The development after equation (15) is based upon a different conception than that of Butler and does not involve certain numerical approximations made by him.

If a molecule of volume $\delta v$ is brought from an infinite distance where the electrostatic field is zero to a distance $r$ from an ion of charge $z_1 e$ ($e$ is electronic charge, $z_1$ the valence of ion) at which position the field is $E$, then the work done by the electric field is given by the expression

$$\delta v \int_0^E P \mathrm{d}E \qquad (8)^5$$

Since $P$ is the polarization per unit produced by the field, it is proportional to it, so that

$$P = \alpha E \qquad (9)$$

where the proportionality factor is the susceptibility and is a constant for isotropic media.[6] $\alpha$ is related to the dielectric constant, $D$, by the equation

$$D = 1 + 4\pi\alpha \qquad (10)$$

From equations (8) and (9), the work produced by bringing $\delta v_{II}$ from $\infty$ to $r$ is

$$\delta v_{II} \int_0^E \alpha_{II} E \mathrm{d}E = \alpha_{II}\, \delta v_{II} \frac{E^2}{2} \qquad (11)$$

Now, if the ion is in solvent I, and $\delta v_{II}$ of solvent II is brought to a distance $r$ from it, an equal volume of solvent I must be displaced, and the work done against the electric forces in removing this molecule will be

$$\delta v_{II} \int_0^E \alpha_I E \mathrm{d}E = \alpha_I\, \delta v_{II} \frac{E^2}{2} \qquad (12)$$

Therefore the work done against the electric forces in accomplishing the exchange will be given by

$$(\alpha_I - \alpha_{II})\, \delta v_{II} \frac{E^2}{2} \qquad (13)$$

The potential, $\psi$, at a distance $r$ from the ion is $ez_i/Dr$, and the field is given by

$$E = \frac{\partial \psi}{\partial r} = -\frac{ez_i}{Dr^2} \qquad (14)$$

As a result the work term, $dW$, for this exchange of element of volume, $\delta v_{II}$, is

$$\mathrm{d}W = (\alpha_I - \alpha_{II})\, \delta v_{II} \frac{e^2 z_i^2}{2D^2 r^4} \qquad (15)$$

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[4] Butler, *J. Phys. Chem.*, **33**, 1015 (1929).

[5] Livens, "Theory of Electricity," Chapt. 5, Cambridge University Press, **1918.**

[6] Page, "Introduction to Theoretical Physics," D. Van Nostrand Co., New York, **1928,** pp. 325–336.

$dW$ in equation (15) may be regarded as the work done against the electric forces necessary to change the dielectric constant of the medium at a distance $r$ from the ion by an amount equal to

$$(\alpha_I - \alpha_{II})\,\delta v_{II} = \frac{(D_I - D_{II})}{4\pi}\,\delta v_{II} \tag{16}$$

where $D_I$ and $D_{II}$ are the dielectric constants of solvent I and substance II, respectively. Consequently, if (15) be integrated over the entire volume, we shall obtain the work necessary to change the dielectric constant of the whole medium by that same amount. Therefore

$$dW = \int_{r=a_i}^{r=\infty} (\alpha_I - \alpha_{II})\,\delta v_{II}\,\frac{e^2 z_i^2}{2D^2 r^4}\,4\pi r^2 dr \tag{17}$$

or

$$dW = \frac{e^2 z_i^2}{2D_I^2 a_i}\,4\pi\,(\alpha_I - \alpha_{II})\delta v_{II} \tag{18}$$

where $a_i$ is the ionic radius. In integrating $D$ has been assumed to be constant. This is entirely justifiable since the over-all change in dielectric constant is of the order of an infinitesimal.

If $n_{II}$ is the number of molecules of kind II per cc., the total change in dielectric constant will be

$$4\pi\,(\alpha_I - \alpha_{II})\,\delta v_{II} n_{II} = (D_I - D_{II})\,\delta v_{II} n_{II} = D_I - D \tag{19}$$

where $D$ is the dielectric constant of the solution. The total work in bringing about this change is given by the expression

$$W = \frac{e^2 z_i^2}{2a_i}\,4\pi\,(\alpha_I - \alpha_{II})\,\delta v_{II} \int_0^{n_{II}} \frac{dn_{II}}{D^2} \tag{20}$$

if the substance is brought up bit by bit in a medium of varying dielectric constant $D$.

This equation may be integrated since as a first approximation we may represent $D$ as a linear function of $n_{II}$, or $D = D_I - Bn$, where $B$ is a constant, and $n$ is the number of moles per cc. Equation 20 becomes

$$\begin{aligned} W &= \frac{e^2 z_i^2}{2a_i}\,4\pi\,(\alpha_I - \alpha_{II})\,\delta v_{II}\,N \int_0^n \frac{dn}{(D_I - Bn)^2} \\ &= \frac{e^2 z_i^2}{2a_i}\,4\pi\,(\alpha_I - \alpha_{II})\,\delta v_{II}\,\frac{N}{B}\left(\frac{1}{D_I - Bn} - \frac{1}{D_I}\right) \\ &= \frac{e^2 z_i^2}{2a_i}\,4\pi\,(\alpha_I - \alpha_{II})\,\delta v_{II}\,\frac{N}{B}\left(\frac{1}{D} - \frac{1}{D_I}\right) \end{aligned} \tag{21}$$

upon introducing these relations if $N$ is Avogadro's number. From (16), $4\pi\,(\alpha_I - \alpha_{II}) = D_I - D_{II}$, where $D_I$ and $D_{II}$ are the dielectric constants of the pure substances I and II, respectively. Further, $\delta v_{II} N$ equals the molecular volume, $M/d$, and $B$ equals $(D_I - D_{II})/n'_{II}$ where $n'_{II}$ is the number of moles of pure substance II in 1 cc., or $n'_{II} = d/M$. Hence $B = [(D_I - D_{II})/d]M$. Upon substitution of these relations in (21), we obtain

$$W = \frac{e^2 z_i^2}{2a_i}\,(D_I - D_{II})\,\frac{M}{d}\,\frac{d}{M(D_I - D_{II})}\left(\frac{1}{D} - \frac{1}{D_I}\right) = \frac{e^2 z_i^2}{2a_i}\left(\frac{D_I - D}{DD_I}\right) \tag{22}$$

The same equation may be obtained more simply if not so rigorously from equation (18), if we regard $4\pi\ (\alpha_I - \alpha_{II})\delta v_{II}$ to represent an infinitesimal lowering of dielectric constant, $-dD$, produced by one molecule of volume $\delta v_{II}$. If this is constant, the lowering of the dielectric constant is a linear function of the number of moles, $n$. Therefore

$$W = \frac{e^2 z_i^2}{2a_i}\int_{D_I}^{D} -\frac{dD}{D^2} = \frac{e^2 z_i^2}{2a_i}\left(\frac{1}{D} - \frac{1}{D_I}\right) \qquad (22)$$

We have calculated the work against the electric forces corresponding to bringing a volume $n_{II}\delta v_{II}$ of $n_{II}$ molecules of substance II into the solution which replace an equal volume of solvent I. This is identical but opposite in sign with the work done by the electric forces, $W_e$, when the ion is transferred from solvent I to a solution containing $n$ molecules of substance II. Therefore, according to thermodynamics

$$-W_e = \Delta\bar{F} = kT \ln \frac{\gamma}{\gamma_I} = \frac{e^2 z_i^2\, 4\pi\,(\alpha_I - \alpha_{II})\,\delta v_{II} n_{II}}{2a_i\, DD_I} \qquad (23)$$

where $\gamma$ and $\gamma_I$ are the activity coefficients of the ion in the solution and pure solvent I, respectively, and $\Delta\bar{F}$ is the partial free energy of transfer.[7] From the latter point of view, equation (22) is seen to be that developed by Born[8] from considerations involving ion transfer. The above deduction is more detailed from an electrostatic point of view than that of Born, and throws further light upon the mechanism of the medium changes.

In some of the following calculations, it is numerically simpler and sufficiently accurate to put $DD_I$ in (23) equal to $D_I^2$. Upon this basis it is clear that (23) becomes

$$-W_e = \frac{e^2 z_i^2}{2a_i\, D_I^2}\, 4\pi\,(\alpha_I - \alpha_{II})\,\delta v_{II} n_{II} = \frac{e^2 z_i^2}{2a_i\, D_I^2}(D_I - D) = kT \ln \frac{\gamma}{\gamma_I} \qquad (24)$$

This latter expression will be found very useful and simple for computing many of the results.

Returning now to the theory of homogeneous catalysis, if we consider a reaction to take place between a neutral molecule and an ion, we obtain from equations (1) and (2)

$$\bar{k} = \bar{k}_0 m_i \gamma_n \gamma_i\, F' = \bar{k}_0 m_i F \qquad (25)$$

Further, from equation (23), we found that the effect of the medium upon the activity coefficient of one species is given by

$$\frac{\gamma}{\gamma_I} = e^{-W_e/kT}$$

Since $F$ is a function of the "$\gamma$'s," this latter equation and equation (25) permit us to write equation (7) in the more definite form

$$\bar{k} = \bar{k}_0 m_i\, e^{-nW_e/kT} \qquad (26)$$

[7] We speak of individual ion activity coefficients at this time. In applying this equation, activity coefficient products and ratios should probably be employed.

[8] Born, *Z. Physik*, **1**, 45 (1920).

where $W_e$ is defined by (23), and $n$ is an integer depending upon the number of species involved. If we anticipate our examination of the data of many reactions, we find that $n$ is usually 1, although we have found a case where it appears to be $-1$. Sometimes $W_e$ is very small so that $n$ appears to be zero.

**Calculation of the Secondary Kinetic Effect Caused by Change of Medium upon the Velocity of Hydrolysis of Ethyl Orthoformate.**—The hydrolysis of ethyl orthoformate is so sensitive to hydrogen ions that buffered solutions such as acetic acid–sodium acetate mixtures must be employed. Consequently, there will be a secondary medium effect due to the decrease in the concentration of the hydrogen ion produced by the change of medium. Since for acetic acid in any medium at constant temperature and pressure, the thermodynamic equilibrium condition is expressed by $K = (\gamma_H\gamma_{AC}/\gamma_{HAC})\ (m_H m_{AC}/m_{HAC})$, and since $m_{AC}/m_{HAC}$ is a constant in the case of the solutions under consideration, we find that in the two media the hydrogen-ion concentration ratio is given by

$$\frac{m_{HI}}{m_H} = \frac{\gamma_H\gamma_{AC}\ \gamma_{HAC_I}}{\gamma_{H_I}\gamma_{AC_I}\ \gamma_{HAC}} = \frac{\gamma_H\gamma_{AC}}{\gamma_{H_I}\gamma_{AC_I}} \tag{27}$$

if we neglect the small change in the activity coefficient of the undissociated molecule produced by the molecular, not the ionic, fields. Since the velocity constant due to this secondary effect is proportional to the hydrion concentration, $\frac{\bar{k}_0}{\bar{k}} = m_{HI}/m_H$, and consequently from equations (24) and (27)

$$\ln \bar{k}_0 - \ln \bar{k} = \ln m_{HI} - \ln m_H = \frac{e^2}{D_I{}^2 a_i kT}(D_I - D) = \frac{-2W_e}{kT} \tag{28}$$

Substituting $4.77 \times 10^{-10}$ e. s. u., 78.8, $1.37 \times 10^{-16}$ ergs for $e$, $D_I$ and $k$, respectively, and employing 1.5 Å. as a probable value for the mean value of the hydrogen and acetate ions, we obtain

$$\ln \bar{k}_0 - \ln \bar{k} = 0.06(D_I - D) \tag{29}$$

Harned and Samaras[9] have shown that in the case of seven solvents the experimental results yield

$$\ln \bar{k}_0 - \ln \bar{k} = 0.07(D_I - D) \tag{29a}$$

For simplicity, the approximate equation (24) has been employed. If the more exact equation (23) had been used

$$\ln \bar{k}_0 - \ln \bar{k} = \frac{0.06\ D_I{}^2}{DD_I}(D_I - D) \tag{29b}$$

would have been obtained. For the data in question, and owing to the uncertainty involved in the assigned value of $a_i$, (29) is as numerically valid as (29b).

Thus we may interpret the data by a secondary medium effect which in terms of the velocity constant is expressed by

$$\bar{k} = \bar{k}_0\, e^{2W_e/kT}$$

[9] Harned and Samaras, THIS JOURNAL, **54**, 1 (1932).

On the other hand, this computation does not exclude a primary medium effect. Although we believe the factor of greatest importance and magnitude has been computed, we cannot in view of the lack of data determine how or whether the kinetic factor, $F$, varies with the changing character of the medium. Our result indicates a small primary effect. This is substantiated by the data of Manning,[10] who found that dextrose had no effect on the velocity of hydrolysis of ethyl formate, and by Robinson,[11] who showed that 1.68 $M$ dextrose had no appreciable effect on the velocity of hydrolysis of ethyl acetate when catalyzed by 0.1 $M$ hydrochloric acid.

**A Calculation of Two Primary Medium Effects.**—Prasad and Godbole[12] have measured the velocity constant of the reaction,

$$CH_3I + Na_2S_2O_3 = NaCH_3S_2O_3 + NaI$$

in mixtures of water and methyl, ethyl, isopropyl and $n$-propyl alcohols. The plots of log $\bar{k}$ against the weight per cent. of alcohol are straight lines, using the extrapolated log $\bar{k}_0$ values, up to concentration of 10, 20, 30 and 60%, for the solutions of $n$-propyl, isopropyl, ethyl and methyl alcohols, respectively. Above these concentrations, there is a sharp decrease in log $\bar{k}$ which these investigators ascribed to compound formation. In Table I are given the results read from plots of their data which show the increase in velocity caused by the addition of 20% of the alcohols in question.

TABLE I

SHOWING COMPUTATION OF EXPERIMENTAL CONSTANT OF EQUATION 30

| Alcohol | $\ln \bar{k} - \ln \bar{k}_0$ | $D_I - D$[13] | $\frac{\ln \bar{k} - \ln \bar{k}_0}{D_I - D}$ |
|---|---|---|---|
| Methyl (20%) | 0.47 | 9.8 | 0.05 |
| Ethyl (20%) | .68 | 11.9 | .06 |
| Isopropyl (20%) | .80 | 13.2 | .06 |
| $n$-Propyl (20%) | .83 | 13.9 | .06 |

The column headings are self-explanatory. The experimental results lead to

$$\ln \bar{k} - \ln \bar{k}_0 = 0.06(D_I - D)$$

which is in accord with the primary factor in equation (26) when $n$ equals $+1$, and where $W_e$ is given by equation (25). For monovalent ions, $W_e/kT = 0.03(D - D_I)$, but in the case of a unibivalent salt, $-W_e/kT = 0.06(D_I - D)$, if $a_i$ is taken to be 1.5 Å. The valence factor is $\Sigma z_i^2/\nu$ where $\nu$ is the number of ions formed from one molecule of electrolyte. Thus, the kinetic factor is given by $e^{-W_e/kT}$.

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

[11] Robinson, *Trans. Faraday Soc.*, **26**, 217 (1930).

[12] Prasad and Godbole, *J. Ind. Chem. Soc.*, **7**, 127 (1930).

[13] For sources of dielectric constant lowerings, see Harned and Samaras, THIS JOURNAL, **54**, 1 (1932).

The above agreement should be considered as qualitative rather than quantitative because of the insufficient number of points given by the investigators, and also because the extrapolated zero value and not the experimental one was used in deriving the values shown in Table I.

From a quantitative viewpoint the thorough investigations of Fontein[13a] on the transformation of acetylchloroaminobenzene and related compounds by 0.2 $N$ hydrochloric acid in water–alcohol mixtures are of great interest as a test of equation (26). When the $\log \bar{k} - \log \bar{k}_0$ values for the transformation of acetylchloroaminobenzene in water–methyl alcohol solutions are plotted against $(1/D - 1/D_I)$, a straight line is obtained for all the mixtures with a slope equal to 174; the methyl alcohol concentration is as high as 83.3 weight per cent. The velocity constants of the transformations of formylchloroaminobenzene, acetylchloroaminobenzene, propionylchloroaminobenzene, butyrylchloroaminobenzene, benzoylchloroaminobenzene, acetylchloroamino-*m*-methylbenzene and acetylchloroamino-*m*-chlorobenzene have been determined in water–ethyl alcohol mixtures. The $\log \bar{k} - \log \bar{k}_0$ values for a given alcohol concentration were found to be practically the same and were therefore averaged for all seven substances and the mean values plotted against $(1/D - 1/D_I)$; the slope of the resulting straight line is 142. Thus we have

$$\ln \bar{k} - \ln \bar{k}_0 = 327 \left(\frac{1}{D} - \frac{1}{D_I}\right)$$

From equations (26) and (23), taking again $n = 1$

$$\ln \bar{k} - \ln \bar{k}_0 = \frac{\epsilon^2}{2akT} \left(\frac{1}{D} - \frac{1}{D_I}\right) = 330 \left(\frac{1}{D} - \frac{1}{D_I}\right)$$

For hydrochloric acid the value of $a$, which is defined by

$$\frac{1}{a} = \frac{1}{2}\left[\frac{1}{a_{H^+}} + \frac{1}{a_{Cl^-}}\right]$$

is $0.85 \times 10^{-8}$ from the values of ionic radii given by Bragg and Pauling.[13b] The agreement between the theoretical and experimental slopes leaves little to be desired in the case of water–ethyl alcohol mixtures; for the transformation of acetylchloroaminobenzene in water–methyl alcohol solutions the experimental slope is high, being 400.

**A Calculation of a Primary Salt Effect.**—We shall now consider the iodide-ion catalysis of hydrogen peroxide, and compute the primary medium effect produced by salt addition. To do this, we shall employ the same considerations and assume that the salt effect is a function of the change in dielectric constant of the medium just as in the previous cases where the influence of the change in medium upon the reaction velocity has been shown to be a function of a measured change in dielectric constant.

[13a] Fontein, *Rev. Trav. Chim.*, **47**, 635 (1928).

[13b] Bragg, *Phil. Mag.*, [6] **40**, 169 (1920); Pauling, THIS JOURNAL, **49**, 765 (1927).

It is well known that the measured activity coefficients, $\gamma$, of an electrolyte may be represented by Hückel's equation,[14] or

$$\log \gamma = - \frac{u \sqrt{\Gamma}}{1 + A \sqrt{\Gamma}} + B\Gamma - \log (1 + 0.018\, vm) \qquad (30)$$

$u$ is the universal constant of the Debye and Hückel theory, $A$ allows for the sizes of the ions, and from it the mean distance of approach of ions may be computed. The logarithmic term on the right allows for the purely formal relation between the activity coefficient, $f$, defined by $a/N$ where $a$ is the activity and $N$ is the mole fraction and $\gamma$, or $a/m$ where $m$ is the molality. Further, $\Gamma$ equals $\Sigma c_i z_i^2$, where $c_i$ is the concentration of an ion in moles per liter of solution and the summation is for all the ions. $B$ was assumed by Hückel to be caused by the change in dielectric constant of the medium brought about by the addition of the electrolyte. Hückel assumes that this variation is linear according to the law, $D_0 - D = \Sigma \delta_i c_i$, where $\delta_i$ is a constant characteristic of an ion and the summation is for all the ions. Hückel obtains his value for $B$ by computing the effect of change in dielectric constant upon the charging process of the ion and subsequently the related influence upon the activity coefficient. This method leads to a linear variation of the logarithm of $\gamma$ which agrees with the observed results but, as pointed out by Harned,[15] the predicted lowering of the dielectric constant is much too great, in fact so great that the dielectric constant would become negative in some electrolytic solutions at 4 $M$ concentration.

By considerations which involve the salting out effect of ions, Butler obtained

$$\ln f_{12} = \frac{e^2}{2kTD^2} \frac{4\pi (\alpha_I - \alpha)\, \delta v\, N}{1000 \times a} \Gamma = 2.3\, B\Gamma \qquad (31)$$

$f_{12}$ is that part of the activity coefficient which is caused by the fact that the solvent molecules because of their polar nature congregate around an ion, thereby displacing or "salting out" other ions; $a$ is the mean ionic radius, $\alpha$ is the average value of the susceptibility of the ions of the salt, $\alpha_I$ the susceptibility of water, so that $4\pi (\alpha_I - \alpha)\, \delta v$ is the average lowering of the dielectric constant produced by one ion per cc. Therefore

$$\frac{4\pi (\alpha_I - \alpha)\, \delta v\, N}{1000} \Sigma m_i = D_I - D \qquad (32)$$

or the total lowering of the dielectric constant.

Equation 23 was obtained from the process of bringing a molecule of substance II up to the ion and replacing a molecule of substance I. Similarly, we can bring the ions of a salt to the neighborhood of an ion and replace the solvent, and an equation will be obtained identical with (23) with the exception that we must now use mean values. If this is done we

[14] Hückel, *Physik. Z.*, **25**, 93 (1925).

[15] Harned, THIS JOURNAL, **48**, 326 (1926).

may readily obtain from (23) the following expression for $W_e$ (for a binary electrolyte)

$$-\frac{W_e}{kT} = \frac{z_+z_-e^2}{2akT}\frac{(D_I - D)}{DD_I} = \frac{4\pi(\alpha_I - \alpha)\delta v N e^2}{2akT\, DD_I\, 1000}\Gamma = 2.3B\Gamma \qquad (33)$$

which is identical with (31) except that we have $DD_I$ in the denominator instead of $D^2$. $W_e$ is to be interpreted as the work done by the electrical forces in bringing up from an infinite distance the salt, ion by ion, to a distance $a$ from an ion until the dielectric constant is $D$, or, more simply, $-W_e$ may be looked upon as the electrical energy gained by transfer of an ion from a medium of dielectric $D_I$ to one of $D$.

According to the theory, since there is no secondary salt effect, the kinetic factor is given by $e^{-W_e/kT}$ and the velocity constant by $\bar{k} = \bar{k}_0 e^{-W_e/kT}$ [using (26) and taking $n$ equal to 1], where $\bar{k}_0$ is the velocity constant in the solution before the salt addition. Thus we find from equations (26) and (33) that

$$\ln \bar{k} - \ln \bar{k}_0 = 2.3B\Gamma \text{ or}$$
$$\log \bar{k} - \log \bar{k}_0 = B\Gamma \qquad (34)$$

It has already been pointed out by French,[16] and by Harned and Åkerlöf[17] in previous discussions of the iodide ion catalysis of hydrogen peroxide that the neutral salt effects follow the order of the $B$ constants. That equation (34) is valid is shown clearly in Table II. Log $\bar{k}$ − log $\bar{k}_0$ was plotted for each salt against the concentration of salt. The slopes were determined for each of the salts listed and are given in the second column. The third column contains $B\Gamma/c$, where the $B$ values were obtained from electromotive force measurements of the activity coefficients.[18]

TABLE II

VERIFICATION OF EQUATION 34

| Salt | $\frac{\log \bar{k} - \log \bar{k}_D}{c}$ | $\frac{B\Gamma}{c} = 2B$ |
|---|---|---|
| NaBr | 0.080 | 0.080 |
| KBr | .036 | .040 |
| KCl | .028 | .034 |
| NaCl | .062 | .064 |
| LiCl | .139 | .140 |
| | | $\frac{B\Gamma}{c} = 6B$ |
| $K_2SO_4$ | −0.019 | −0.094 |
| $Na_2SO_4$ | .020 | − .030 |
| $Li_2SO_4$ | .074 | .052 |
| $BaCl_2$ | .29 | .23 |
| $SrCl_2$ | .26 | .29 |

[16] French, *J. Phys. Chem.*, **32**, 401 (1928).

[17] Harned and Åkerlöf, *Trans. Faraday Soc.*, **24**, 666 (1928).

[18] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926). Harned, THIS JOURNAL, **51**, 416 (1929).

The agreement between the theory and the experimentally derived results is excellent for the uni-univalent salts. For the unibivalent salts it is not so good, but it should be observed that any error in $B$ is multiplied by 6, and in these cases the $B$ constants are not as well known. Further, we observe that the order of the results is correct for the sulfates, and that potassium sulfate with a negative $B$ constant decreases the velocity.[19]

It is seen from equations (33) and (34) that the experimental results show that the velocity constant depends upon the dielectric constant lowerings produced by the ions of the various salts; in other words, the velocity constant is a function of the transfer of ions and not the neutral hydrogen peroxide molecule. If we consider homogeneous catalysis, in general, it is not only conceivable but probable that in many cases it will be necessary to take into account the transfer of the neutral substrate molecule if this condition be required by the mechanism of the reaction. The activity coefficient of the neutral molecule in the salt solution, as given by Butler, is

$$\ln \gamma_B = \frac{4\pi (\alpha_I - \alpha_B) \delta v_B e^2 N}{2kT D^2 1000} \Sigma \frac{m_i z_i^2}{a} = -\frac{W_e'}{kT} \qquad (35)$$

This equation is identical with that of Debye and MacAulay[20] with the exception that $D^2$ and not $D_I^2$ appears in the denominator. Our treatment would lead to $DD_I$. It is apparent that $\ln \gamma_B$ depends on $(\alpha_I - \alpha_B)$, the concentration of ions, and the values of $a_i$ of the salts. Thus, if the susceptibility of the reacting substance is the same as that of water, $\gamma_B$ does not change upon salt addition. In the reaction under consideration any change in $\gamma_B$ is small since the dielectric constant of a solution of 45% hydrogen peroxide is only 2.5% higher than water. Therefore in the iodide-ion catalysis of hydrogen peroxide this complicating factor does not enter to an appreciable extent, a conclusion which may account for the validity of equation (34).

Although we cannot be expected to achieve exact results with a theory as approximate as the one we have used, we have obtained valuable support of the contention that the linear salt effect and the linear kinetic salt effect are both functions of the change in dielectric constant of the medium produced by salt addition, since we have employed the same theory for both salt effects and medium effects involving known changes in the dielectric constant.

Before we leave the discussion of the iodide-ion catalysis of hydrogen peroxide, we shall point out an interesting fact which so far we have been

[19] The correction of the first member on the right of equation (30) due to the development of the Debye and Hückel theory by Gronwall, La Mer and Sandved [*Physik. Z.*, **29**, 358 (1928)] in the case of bivalent electrolytes will unquestionably alter the $B$-values.

[20] Debye and MacAulay, *ibid.*, **26**, 22 (1925).

unable to explain. Bohnson[21] has determined the velocity constants of this reaction in water and in mixtures of water with glycerin, ethyl and methyl alcohols. Up to concentrations of 30% of these compounds $\ln \bar{k} - \ln \bar{k}_0$ equals a constant times the molality of the organic solvent. In Table III are given the values of $\ln \bar{k} - \ln \bar{k}_0$, $D_0 - D$ at 20 wt.% organic solvent concentration, and the slope of the plot of $\ln \bar{k} - \ln \bar{k}_0$ against $D_0 - D$.

TABLE III

CONSTANTS OF EQUATION 30 FOR THE IODIDE-ION CATALYSIS OF HYDROGEN PEROXIDE IN ORGANIC SOLVENTS

| Solvent | $\ln \bar{k} - \ln \bar{k}_0$ | $D_0 - D$ | $\frac{\ln \bar{k} - \ln \bar{k}_0}{D_0 - D}$ |
|---|---|---|---|
| Methyl alcohol (20%) | −0.471 | 9.8 | −0.048 |
| Ethyl alcohol (20%) | − .530 | 12.0 | − .044 |
| Glycerin (20%) | .223 | 4.4[a] | .051 |

[a] Estimated from audio frequency.

Although the numerical values are of the expected order of magnitude, there is a decrease of reaction velocity in the case of the alcohols and an increase in glycerin solutions. We can merely state this result without further explanation by equation (26), where $n$ is $+1$ for glycerin solutions and $-1$ for methyl and ethyl alcohol solutions if $a_i$ is taken to be 1 Å., and $n$ is $+2$ or $-2$, respectively, if $a_i$ is 2 Å.

**The Relation of the Simple Theory to the More Complicated Cases of Homogeneous Catalysis.**—We have now to consider briefly two examples of homogeneous catalysis which cannot be computed by the theory in its simple form and for the present we shall limit the discussion to showing that in these cases the difficulties reside in the computation of $W$ in equation (7), in other words, our simple calculation of $W_e$ and $W_e'$ does not suffice.

From the data on the neutral salt catalysis of ethyl acetate, Harned and Åkerlöf[22] have pointed out and Robinson has verified with eleven salts that the velocity constant, $\bar{k}_0$, of hydrolysis of ethyl acetate with 0.1 $N$ hydrochloric acid in salt solutions is related to that, $\bar{k}_0$, in the 0.1 $N$ hydrochloric acid solution by the equation

$$\bar{k} = \bar{k}_0 \gamma_e^{1/2} \tag{36}$$

where $\gamma_e$ is the activity coefficient of the ester as determined from solubility measurements. Thus

$$\ln \bar{k} - \ln \bar{k}_0 = \tfrac{1}{2} \ln \gamma_e = -\tfrac{1}{2} \frac{W_e'}{kT}$$

or

$$\bar{k} = \bar{k}_0 e^{-1/2 W_e'/kT} \tag{37}$$

[21] Bohnson, *J. Phys. Chem.*, **24**, 677 (1920).

[22] Harned and Åkerlöf, *Trans. Faraday Soc.*, **24**, 666 (1928); Robinson, *ibid.*, **26**, 217 (1930).

In this case, however, $\gamma_e$ may not be computed completely for the salts in question by the Debye and MacAuley equation or equation (35). For example, $\gamma_e$ in lithium iodide solutions is less than in water, a result which is entirely in disagreement with the calculation. In this case the fault lies in the fact that all the required factors have not been employed in the calculation of $W_e'$ in equation (35).

The hydroxyl-ion catalysis of decomposition of diacetone alcohol, which has been studied very comprehensively by Åkerlöf, offers quite a different and even more interesting case which we are unable to calculate by the simple theory. Åkerlöf[23] showed that, in general, the velocity constant changes caused by changes of concentration of the hydroxide catalysts as well as the addition of various salts to the catalysts at constant concentration paralleled the behavior of the activity coefficients of the hydroxides.[24] Consequently, we have evidence that $W$ in the kinetic factor in equation (7) is to a large extent a function of the transfer of the ions of the hydroxides. The actual calculation of this work term has not been made since it involves further considerations than those yet employed in the computation of $W_e$. The unmodified theory is unable to account for the peculiarities of the solutions containing the hydroxyl ion.[25]

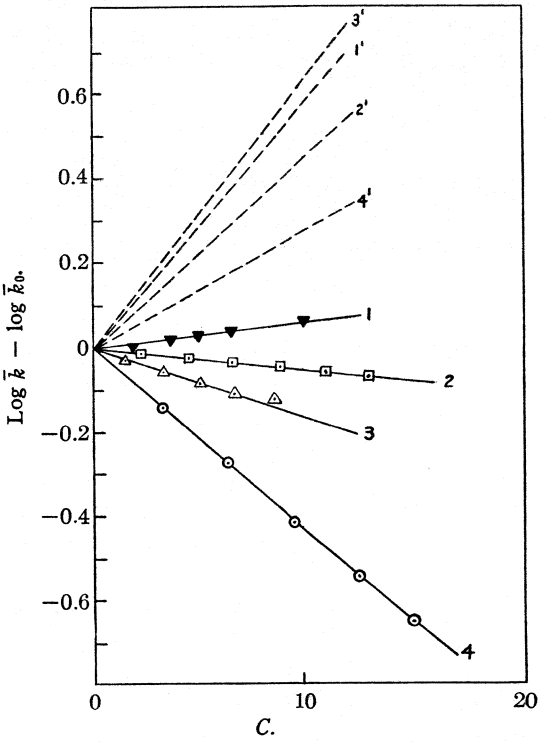


Fig. 1.—Theoretical and observed log $\bar{k}$ − log $\bar{k}_0$–$C$ plots for the decomposition of diacetone alcohol in water–alcohol mixtures: 1–1′, isopropyl; 2–2′, ethyl; 3–3′, *n*-propyl; 4–4′, methyl.

A consideration of the effect of change of medium upon the hydroxide-ion catalysis of diacetone alcohol indicates one additional factor. In Fig. 1,

[23] Åkerlöf, THIS JOURNAL, **48**, 3046 (1926); **49**, 2955 (1927); **50**, 1272 (1928); **51**, 984 (1929).

[24] Harned and Åkerlöf, *Trans. Faraday Soc.*, **29**, 666 (1928).

[25] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); Harned, Chap. XII in Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, **1930**.

$\log k - \log k_0$ in mixtures of water and some alcohols has been plotted against $C$, the concentration of alcohol in moles per 1000 g. of solution and is represented by the full lines. It is important to note that in all cases the plots are straight lines to concentrations as high as 50 wt.% alcohol, and for methyl alcohol up to 100%. The theoretical results computed from the equation, $\ln \bar{k} - \ln \bar{k}_0 = -W_e/kT$, where $W_e$ is derived from equation (24), are represented by the dashed lines. We see that the order is the same with the exception of that of *n*-propyl alcohol. The additional factor which may account for the observed decreases rather than the predicted increases of $k$ is possibly the formation of alcoholate ions of lower catalytic activity than the hydroxyl ion.

In conclusion, the empirical relation proposed by Grube and Schmid,[26] $\bar{k} = \bar{k}_0 \times 10^{r \cdot c}$, for the effect of neutral salts upon the velocity constant of hydrolytic reactions, should be mentioned. Since $r$ and $C$ are a specific constant and the normal concentration of the salt, respectively, it is obvious that this expression is similar to our equations by means of which we have attempted to evaluate $r$ in some cases.

More recently Gross[27] concluded that at least in some reactions between an ion and a neutral body, $\gamma_A/\gamma_{AB}$ in equation (3) is unity, and derived an expression for the activity coefficient of the neutral substance, $\gamma_B$, in a salt solution. It may be easily shown that his expression for $\gamma_B$ can be obtained from (13) by Butler's procedure, if the total Debye and Hückel potential, which involves both the potential due to the ion itself and that due to the interionic forces, instead of the ion potential alone is used. These more complicated aspects of the problem will be taken up in a further communication.

## Summary

1. In this study we have attempted to express the kinetic factor, $F$, for medium effects in homogeneous catalysis by $e^{-W/kT}$ and have sought a value of $W$ which is consistent with electrostatics and the experimental results. For examples in which complicating factors such as change of catalyzing ion, etc., are avoided, we have found that $W$ may be represented with a fair degree of approximation by equations (23) or (24), and (33). This work term is associated with the dielectric constant change produced by a neutral substance or a salt.

2. The secondary medium effect of the hydrolysis of ethyl orthoformate catalyzed by acetic acid–sodium acetate buffer solutions has been successfully computed.

3. The primary medium effect of the reaction between methyl iodide and sodium thiosulfate and the transformations of substituted chloroaminobenzenes are in agreement with the theory.

[26] Grube and Schmid, *Z. physik. Chem.*, **119**, 19 (1926).

[27] Gross, *Monatsh.*, **53–54**, 445 (1929).

4. The primary salt effect upon the iodide-ion catalysis of hydrogen peroxide agrees remarkably well with the theoretical prediction.

5. The hydrogen-ion catalysis of ethyl acetate and the hydroxide-ion catalysis of decomposition of diacetone alcohol are too complicated to be computed by the simple theory. It is shown, however, that this is due to complicating factors involved in the calculation of $W$.

6. We are quite aware of the many difficulties confronting further advances in the interpretation of this complicated situation and realize that the simple theory is but an approximation. On the other hand, we believe that the factor of greatest importance is known.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

# THE THERMAL DECOMPOSITION OF AMMONIA ON THE SURFACE OF OSMIUM

BY ERIC A. ARNOLD AND ROBERT E. BURK

RECEIVED JUNE 30, 1931 PUBLISHED JANUARY 7, 1932

While there have been many kinetic investigations of catalytic reactions in recent years, it cannot yet be said that there is universal agreement as to the precise function of the catalyst. For a surface reaction, the most likely major action of the catalyst is to lower the energy of activation[1] as compared with the requirement for the corresponding homogeneous reaction, since this is the dominant rate controlling factor for homogeneous reactions.[2] This action of a catalyst would be more evident were it not for the adsorption of products in some cases, which may have the effect of increasing the apparent energy of activation.[3] This action of reaction products may go so far as to crowd the reactant almost completely off the surface and defeat the action of a catalyst which might lower the activational energy requirement to a degree sufficient for rapid reaction.

Thus, in addition to lowering the energy of activation, an effective catalyst must also preserve a suitable adsorption balance between reactants and products.

Osmium was found by Haber and Le Rossignol[4] to be a very effective catalyst for the synthesis of ammonia, and therefore for its decomposition. We have found that the catalyst with a suitable preliminary treatment assumes a constant activity. The thermal decomposition of ammonia on

[1] Sixth Report of the Committee on Contact Catalysis, *J. Phys. Chem.*, **32**, 1601 (1928).

[2] "Material chains" would require further elaboration of this generalization.

[3] Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," **1929**, 2d ed., p. 234.

[4] Haber and Le Rossignol, *Z. Elektrochem.*, **19**, 53 (1913).

osmium seemed, therefore, a suitable case for establishing experimentally the adsorption balance for an effective catalyst.

## Experimental Procedure

The apparatus used in carrying out the reactions is shown in Fig. 1. The pump system, not shown in the sketch, consisted of a two-stage mercury diffusion pump backed by an oil pump. The supply of liquid ammonia, kept in cylinder A, was purified by passing over barium oxide to remove moisture and condensed in storage bulb C, which was surrounded with liquid air. The ammonia was alternately frozen and liquefied several times, the solid ammonia being pumped each time to remove fixed gases held in solution.

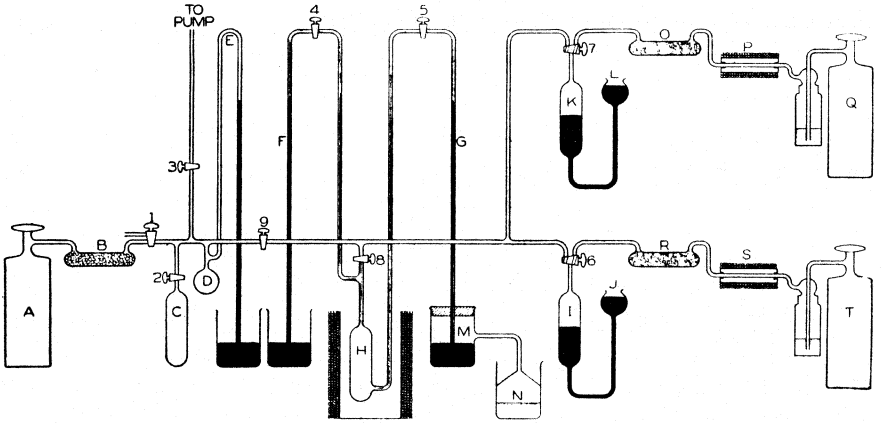


Fig. 1.

The hydrogen for retarding experiments was electrolytic hydrogen from a commercial cylinder T. It was purified by passing through concentrated sulfuric acid and then over finely divided copper maintained at a temperature of approximately 700° by a furnace S and finally over phosphorus pentoxide. The purified hydrogen was stored over mercury in bulb I. The storage bulb was filled and discharged three times in order to remove completely foreign gases which it previously contained.

The nitrogen, obtained from a commercial cylinder and purified in a train similar to that just described, was stored in bulb K.

Considerable difficulty was experienced, especially in the case of the faster reactions, in estimating the initial pressure in the reaction bulb. This difficulty was circumvented by means of the bulb D, which served as a measuring pipet. The pressure readings on barometer E obtained by means of a cathetometer, together with a previous calibration using hydrogen, enabled an accurate estimate of the initial ammonia pressure in the reaction bulb to be made.

The reaction bulb itself was made of quartz. At the outset, the minimum temperature was determined at which the quartz surface itself catalyzed the decomposition of ammonia. This temperature was found to be 610° and was verified from time to time during the course of the investigation.

All temperatures were measured with a platinum to platinum–rhodium thermocouple and a Leeds and Northrup Type K potentiometer. The couple was calibrated at the melting points of silver, zinc, antimony, lead and tin.

The osmium used was in the powdered form and was obtained from the American Platinum Works, its purity being given as better than 99.5%.

Some preliminary experiments indicated a slowly increasing activity of the catalyst. To drive this process of autoactivation to its limit in a reasonable time, the catalyst was seasoned by allowing the ammonia to flow in a slow stream through the reaction bulb with stopcock 5 opened. By regulating the heights of the mercury in the barometer wells the gas could be made to flow continuously over the catalyst and out of barometer G. It was found that after forty-eight hours of seasoning in this way, the activity of the catalyst was constant and results reproducible. The activity of the catalyst was frequently checked by running control reactions especially when the retarding effect of products was being investigated when control reactions were run between each pair of retarded reactions.

The last reaction of each day was allowed to run overnight and the reading next morning taken as the equilibrium reading. This continuous (day and night) operation of the furnace made for close temperature control. It is known that the equilibrium point for this reaction coincides with almost complete decomposition and the amount of ammonia that could be accounted for the next morning was always better than 95% of the ammonia added. Further, since the end-point was obtained on a different day from the early part of the reaction, the results speak for the tightness of the apparatus and for the attainment of thermal equilibrium between the thermocouple and the reaction zone.

## Results

**Order of Reaction.**—In order to establish the apparent order of the reaction, a series of reactions was carried out at constant temperature and varying initial concentrations of ammonia. From these data, the half-life was determined graphically. Table I gives a summary of these results and Fig. 2 gives a series of characteristic reaction curves.

TABLE I

SUMMARY OF RESULTS

| Pressure of ammonia initially added, mm. | Temperature, °C. | Half-life, seconds | $n$ from $t_{1/2} = 1/ka^n$ |
|---|---|---|---|
| 52.4 | 338 | 78 | −1.43 |
| 102.7 | 341 | 205 | −1.40 |
| 196.9 | 342 | 512 | −1.52 |
| 293.8 | 342 | 1102 | |

If these values are substituted in the equation

$$t_{1/2} = 1/ka^n \qquad (1)$$

$n$ has a value between −1.4 and −1.5. The ordinary method, therefore, of determining reaction order leads in this case to a negative value of approximately five-tenths, a result for which we know no precedent.

**Temperature Coefficient.**—The energy of activation was next determined by carrying out a series of reactions in which the pressure of am-

monia was held constant while the temperature was varied. In these cases, the half-life was again determined graphically. Table II gives the results so obtained.

TABLE II

RESULTS OF EXPERIMENTS

| Temperature ($T$), °A. | $1/T \times 10^5$ | Half-life ($t_{1/2}$), seconds | Log $t_{1/2}$ | Quarter-life ($t_{1/4}$), seconds | Log $t_{1/4}$ |
|---|---|---|---|---|---|
| 561 | 178.2 | 5970 | 3.776 | 692 | 2.840 |
| 590 | 169.5 | 695 | 2.841 | 99 | 1.996 |
| 614 | 162.9 | 205 | 2.312 | 36 | 1.556 |
| 640 | 155.9 | 37 | 1.568 | 8 | 0.903 |

These data are shown graphically in Fig. 3. As can be seen, the points lie on good straight lines and the best value for the energy of activation

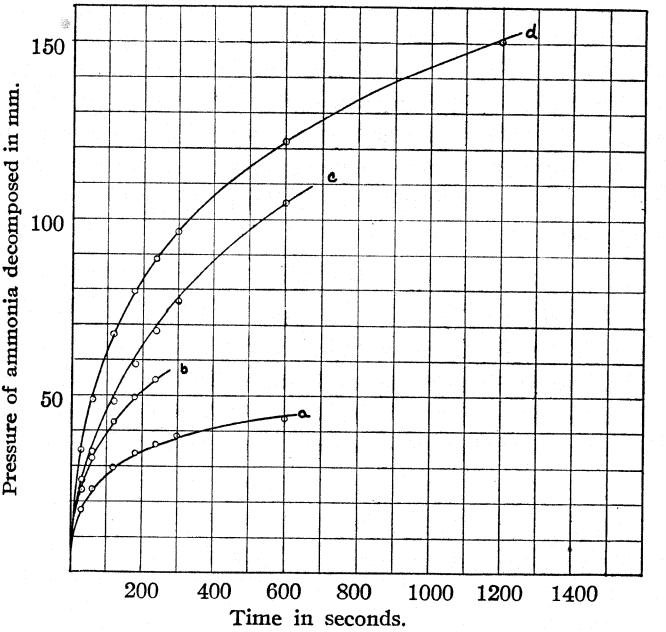


Fig. 2.—The effect of initial pressure on the decomposition of ammonia on osmium at 340°: curve a, initial ammonia pressure, 52.5 mm.; curve b, initial ammonia pressure, 102.7 mm.; curve c, initial ammonia pressure, 196.9 mm.; curve d, initial ammonia pressure, 293.8 mm.

calculated from half-lives and averaged by the method of least squares is 47,600 calories. This same constant evaluated from quarter-lives is 42,200 calories.

**Retarding Effects.**—The separate effects of added nitrogen, hydrogen and mixed nitrogen and hydrogen obtained as products from previous re-

actions were investigated by carrying out series of reactions in which the temperature and initial pressure of ammonia were held constant and the

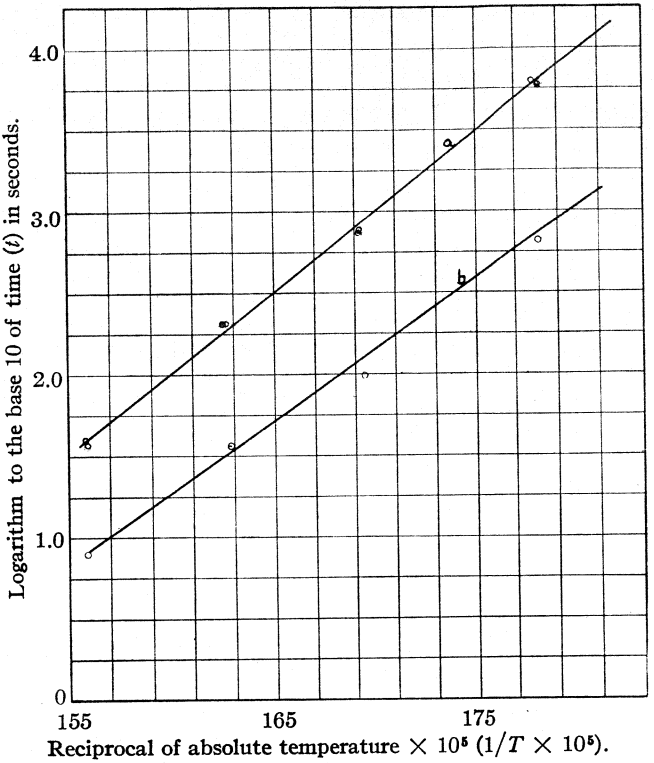


Fig. 3.—Temperature coefficient for the decomposition of ammonia on osmium between 561 and 640° A.; curve a, calculated from half-life; curve b, calculated from quarter-life.

pressure of the retarding gas varied. The results are give in Tables III, IV and V.

TABLE III

RETARDING EFFECT OF NITROGEN

Initial pressure of ammonia, 100 mm. Temperature, 340°

| Pressure of nitrogen initially added, mm... | 0 | 24.6 | 52.4 | 97.9 | 151.2 | 202.3 |
|---|---|---|---|---|---|---|
| Half-life, seconds..... | 205 | 291 | 380 | 565 | 765 | 925 |

TABLE IV

RETARDING EFFECT OF HYDROGEN

Initial pressure of ammonia, 100 mm. Temperature, 340°

| Pressure of hydrogen initially added, mm. | 0 | 24.8 | 51.4 | 100.6 | 150.7 | 198.8 |
|---|---|---|---|---|---|---|
| Half-life, seconds..... | 205 | 405 | 589 | 1025 | 1805 | 3110 |

TABLE V

RETARDING EFFECT OF PRODUCTS FROM PREVIOUS REACTIONS

Initial pressure of ammonia, 100 mm. Temperature, 341°

| | | | | | |
|---|---|---|---|---|---|
| Pressure of products initially added, mm... | 0 | 37.1 | 81.4 | 128.4 | 169.6 |
| Half-life, seconds..... | 205 | 415 | 740 | 1100 | 1610 |

These data are shown graphically in Fig. 4. These curves constitute an excellent check on the purity of the gases used since the retarding effect of products obtained by the decomposition of ammonia in the same bulb can

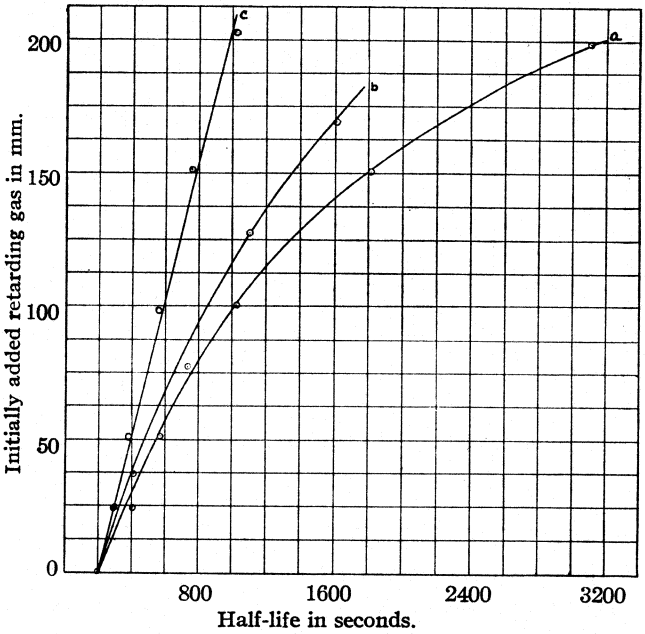


Fig. 4.—Retarding effects of products on the decomposition of ammonia on osmium at 340°: curve a, effect of added hydrogen; curve b, effect of added products; curve c, effect of added nitrogen.

be resolved into two separate retarding effects, one due to nitrogen and one due to hydrogen, and each falls in its proper place on the curves for the individual retarding effects. For instance, in the above table, 128.4 mm. of mercury pressure of products corresponds to partial pressures of hydrogen and nitrogen of 32.1 mm. and 96.3 mm. From the curve for the retarding effect of nitrogen, 32.1 mm. of nitrogen has the same retarding effect as 14.0 mm. of hydrogen. This, then, would make the retarding effect of 128.4 mm. of products equivalent to 110.3 mm. of hydrogen. The observed result taken from the curve is 107.8 mm.

The rate of any heterogeneous gas reaction is a function of the concentration of the reactant in the adsorbed film on the surface and also of the

amount of free surface at any time upon which such adsorption may occur. The rate may therefore be expressed by

$$dx/dt = kf(a - x) \cdot (\text{surface not covered by products}) \qquad (2)$$

where $x$ is the amount of reactant decomposed in any time $t$ and $a$ is the original concentration of the reactant.

In order to evaluate the function of concentration shown in equation (2) for this decomposition, Fig. 5 was drawn from the data for a number of characteristic reactions. The abscissas are the ratios $\Delta P/\Delta t$ where $\Delta t$ is

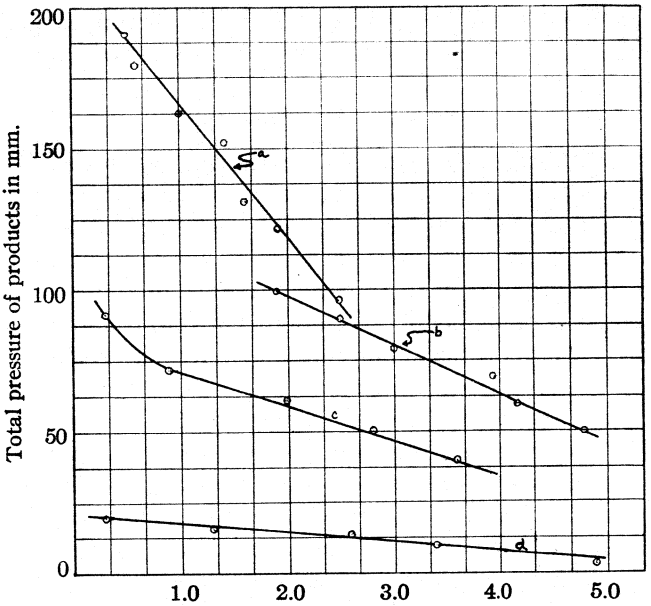


Fig. 5.—Rate of change of pressure–pressure of products for the decomposition of ammonia on osmium: curve a, 100 mm. of ammonia and 81 mm. of products at 340°; curve b, 100 mm. of ammonia and no retarding gas at 338°; curve c, 50 mm. of ammonia and no retarding gas at 316°; curve d, 100 mm. of ammonia and no retarding gas at 271°.

arbitrarily chosen as a twenty-five second time interval and the ordinates are the total pressures of products present. It will be seen that the average curves are all straight lines until near the end of the reaction, even though the pressure of ammonia is changing. This is equivalent to saying that the rate of the reaction is independent of the ammonia concentration and therefore the reaction is of zero order with respect to ammonia. Further, the slope of the lines is a negative one so that the influence of products should be represented by a term of the form

$$(1 - C \cdot \text{pressure of products})$$

The complete rate equation then becomes

$$dx/dt = k(1 - bx) \tag{3}$$

where the symbols have the same significance as before. When this equation is integrated between the limits $x = 0$ and $x = a/2$ and $t = 0$ and $t = t_{1/2}$

$$kt_{1/2} = 1/b \ln(1 - ba/2) \tag{4}$$

The value of $b$ was determined by substitution of values of $t_{1/2}$ and $a$ from Table I and found to be 0.00585. When this value is substituted in equation (4) and the variation of initial pressure of ammonia on the half-life investigated, it is found that the half-life varies directly as the 1.4 power of the original concentration of ammonia. This is in good agreement with the observed result.

## Discussion of Results

When the products of a reaction are so strongly adsorbed that they occupy practically all of the surface and the reactants do not interfere with their adsorption equilibrium which is assumed to be reached, then it may be shown[5] that the apparent order of reaction is one less than that which would prevail if products were absent. We have presented evidence that the decomposition of ammonia on osmium is of zero order on the free surface. Consequently the maximum retarding effect of products might lead to an apparent reaction order of minus one. We have found values between minus four-tenths and minus five-tenths.

Apparently products are somewhat more strongly adsorbed than ammonia. A large part of the active surface is covered with ammonia and this is cut down as the pressure of products increases until at 316° (curve c, Fig. 5) at equal ammonia and product concentrations, about half of the active surface is covered by each. At a lower temperature (curve d, Fig. 5) the relative surface covering shifts over in favor of products. This state of affairs would exist if the heat of desorption of ammonia about equaled the heat of desorption of products, that for products being slightly the greater. That adsorption equilibrium was really reached with respect to products was established by introducing the additional hydrogen and nitrogen into the hot reaction bulb, first with the ammonia and then two hours before the ammonia. The retarding effects were the same in both cases.

In view of these arguments, the observed energy of activation calculated from the half-life—namely, 47,600 calories—is probably close to the true energy of activation and, remarkably enough, is almost equal to the value found by one[6] of us and by Kunsman[7] for the same reaction on tungsten where, for different reasons, the experimental and true values are probably the same.

[5] Hinshelwood, Ref. 3, p. 212.

[6] R. E. Burk, *Proc. Nat. Acad. Sci.*, **14**, 601 (1928).

[7] C. H. Kunsman, THIS JOURNAL, **50**, 2100 (1928).

For an effective catalyst, one should have almost all of the active surface occupied and large covering of the surface by reactants as compared with products, *i. e.*, freedom from poisoning. However, an optimum compromise must exist between these absorptive relations in order that maximum reaction rate may be achieved.

Let the reactants be adsorbed in some given configuration. Reaction on the surface involves an endothermic disturbance of this configuration to give an active state, and then an exothermic transformation from the active state to adsorbed products. If the forces holding the reactants in the initial configuration are too strong, the activating step might become more difficult. This factor must be met in achieving large relative surface covering by reactants, which, if the gas phase concentrations are not too different, would imply a larger heat of adsorption for reactants than for products.

From a kinetic analysis of the thermal decomposition of ammonia on osmium, known to be effective for the reverse reaction, it appears that for the latter the active surface would be almost completely occupied, that the surface (up to more than 50% ammonia concentration in the gas phase) would be largely covered with reactants. This appears to be achieved without the heat of adsorption of reactants (nitrogen and hydrogen) rising much above that for ammonia.

These favorable adsorptive relations follow from the evidence already presented and may be seen to be consistent with the empirical equation (3) representing the velocity of the reaction.

Our experimental rate equation is

$$dx/dt = k(1 - bx)$$

where $x$ is the pressure of ammonia decomposed in any time $t$. If $s$ and $s_1$ are the fractions of the active surface covered with ammonia and products, respectively, when their pressures are $p$ and $p_1$, the adsorption equilibria may be represented by

$$k_1 p(1 - s - s_1) = k_2 s \epsilon^{-h/RT} \qquad (5)$$

for ammonia, and

$$k_3 p_1(1 - s - s_1) = k_4 s_1 \epsilon^{-h'/RT} \qquad (6)$$

for products, where $h$ and $h'$ are the heats of desorption of ammonia and products, respectively. If, as we observed, the rate is of zero order with respect to ammonia, $s \cong 1 - s_1$. Employing this relation and solving equations (5) and (6) simultaneously, taking into account that $p_1 = 2x$ and $p = a - x$, where $a$ is the initial pressure of ammonia, gives

$$s_1 = \frac{2k_2k_3\epsilon^{-h/RT}(x)}{k_1k_4\epsilon^{-h'/RT}(a - x) + 2k_2k_3\epsilon^{-h/RT}(x)}$$

If, as assumed, $\epsilon^{-h/RT} \cong \epsilon^{-h'/RT}$ and $k_1k_4 = 2k_2k_3$, the required relations $s_1 = bx$ and $1 - s_1 = 1 - bx$ would follow, and the experimental rate equation $dx/dt = k(1 - bx)$ would thus be derived.

## Summary

The thermal decomposition of ammonia on pure osmium has been investigated. The reaction was found to be of zero order with respect to ammonia between the temperatures 561 and 640° A. The retarding effect of products is such that the free surface may be represented by a term, 1 − (concentration of products) so that the rate equation becomes

$$dx/dt = k(1 - bx)$$

The energy of activation for the given temperature range calculated from half-lives was found to be 47,600 calories per gram mole and calculated from quarter-lives 42,200 calories.

The physical interpretation of these results is that all gases, both products and reactants, are strongly adsorbed, the latter somewhat more strongly than the former.

Adsorption relations on an effective catalyst have been discussed and compared with those found on the effective ammonia catalyst, osmium.


CLEVELAND, OHIO

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[CONTRIBUTION NO. 79 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

# PHOTOCHEMICAL DECOMPOSITION OF CHLOROFORM

BY DOUGLAS G. HILL

RECEIVED JULY 9, 1931 PUBLISHED JANUARY 7, 1932

The correlation of the absorption spectrum of a substance with its photochemical behavior has been the subject of a number of recent investigations. The present work was undertaken to explain the absorption spectrum exhibited by chloroform, which is of a type which has so far been but little investigated.

A number of absorption spectrograms of chloroform vapor have been taken, using a small Gaertner spectrograph, and a hydrogen discharge tube as a light source. They confirm the work of Massol and Faucon[1] in showing absorption only in the far ultraviolet if the chloroform is sufficiently pure. Under the experimental conditions, using only moderate lengths (50 cm.) of chloroform vapor, the red bands found by Russell and Lepraik[2] and by Ellis[3] would not be expected to appear. The absorption found is apparently perfectly continuous, and extends to the limit of transmission of quartz. The long wave length edge is not sharp, and moves toward longer wave lengths with increasing pressure. At the lowest pressures, less than 1 mm. of mercury, the absorption is recognizable at 2300 Å. and becomes total just below 2100 Å. Even with 1 cm. of liquid chloroform, the edge is not sharp, although much sharper, and falls about 2530 Å.

[1] Massol and Faucon, *Compt. rend.*, **159**, 314 (1914); *Bull. soc. chim.*, **19**, 350 (1916).

[2] Russell and Lepraik, *J. Chem. Soc.*, **39**, 168 (1881).

[3] Ellis, *Phys. Rev.*, **32**, 906 (1928).

Iredale[4] has investigated several alkyl halides, and finds a similar continuous absorption. Herzberg and Scheibe[5] have examined methyl chloride, bromide and iodide very completely, and report a similar continuum, as well as a series of bands still further in the ultraviolet. It is quite possible that similar far ultraviolet bands will be found for many substances, but up to the present so few substances have been investigated in the Schumann region that little is known about them.

The appearance of the continuous absorption is evidence for the dissociation of the molecule. Iredale[6] has shown that this is the case with ethyl iodide, while Bates and Spence[7] have recently confirmed the theoretical evidence offered by Herzberg and Scheibe for the dissociation of methyl iodide. Both these substances give free halogen among the products, so that chloroform affords some interesting differences, not all of which can be explained.

If a quartz bulb containing pure chloroform vapor is exposed to a source of far ultraviolet light, such as a brass arc, neither by measurement of the pressure nor by analysis of the exposed gas for chlorine and hydrogen chloride can any evidence of decomposition be found. But if the vapor is streamed past a source of light, and then over an absorbent, decomposition products are found. The explanation seems to be that organic reaction products are deposited on the window in the static system which absorb the light strongly and prevent the reaction from proceeding to a measurable extent. In the moving vapor the deposit should occur downstream from the window, and reaction be recognizable. As evidence for this explanation, it was found in the measurements that the light transmission of the cell for active wave lengths decreased slowly with exposure, even in the dynamic system. It was necessary to remove and clean it about every six experiments, after which the transparency was substantially as before. This change in transparency was taken into account in the calculations.

The decomposition occurring in a stream of vapor does not give rise to chlorine formation. Hydrogen chloride is the only inorganic product, in agreement with the work of Löb[8] on the decomposition at a hot wire. The quantitative measurements have thus been simplified, and the attempt has been made to elucidate the mechanism of the reaction by a determination of the yield of hydrogen chloride per absorbed light quantum.

## Experimental Procedure

**Purification of Chloroform.**—C. P. chloroform was washed with distilled water to remove the alcohol present (six extractions), dried over calcium chloride, and distilled

[4] Iredale, *Nature*, **126**, 604 (1930).

[5] Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

[6] Iredale, *J. Phys. Chem.*, **33**, 290 (1929).

[7] Bates and Spence, THIS JOURNAL, **53**, 381 (1931).

[8] Löb, *Z. Elektrochem.*, **7**, 907 (1901).

in a stream of hydrogen. It was then frozen at −78.5°, evacuated and twice fractionated in vacuum, at low temperatures. The final product was stored in a blackened bulb behind a mercury filled U-tube of barometric height. The desired amount of vapor was admitted to the apparatus by lowering the mercury in the U-tube so that the chloroform was not allowed to come in contact with the stopcock grease present on the few stopcocks which convenient manipulation demanded, except during the actual filling of the vessel. The chloroform remained extremely pure during the course of the experiments, as shown by the consistency of the results obtained with several preparations, and by the absorption spectrum. Less carefully purified chloroform was apt to show spurious absorption bands in the near ultraviolet.

**Apparatus and Method.**—The brass arc mentioned was used only in the qualitative experiments, since it required constant attention, and was extremely irregular in intensity. Attempts were made to use a hydrogen discharge tube, but were abandoned because of the weakness of the source. Finally a condensed spark was arranged, to use either aluminum or zinc electrodes, placed 1 cm. from the reaction vessel. A blast of air between the spark and the vessel served to protect the latter from the heat evolved, and to keep the metal oxide from collecting on the window.

The reaction chamber was made from a cylindrical vessel of fused quartz with flat ends, divided into two drum-shaped sections, 2 cm. in cross section and 8 mm. in depth by a third window parallel to the ends. The light beam passed down the axis of the cylinder, and the chloroform vapor was streamed through the forward chamber. The rear chamber was filled with the photometer liquid. Since the vessel was constructed in the laboratory, the windows were not perfectly plane, though they were reworked after construction to as nearly plane a surface as possible. In particular, the window between the two chambers was made very thin to minimize light losses.

To define the light beam, a diaphragm with an 8-mm. opening was constructed with black paint on the front window of the vessel. The difficulties in obtaining high intensity in this region of the spectrum made the use of the lens and diaphragm system required to obtain a truly parallel beam of light impractical. It is believed, however, that essentially all of the light was received in the photometer cell. Minor variations in the position of the light source did not affect the results, so it is believed that very little light escaped.

Potassium nitrate solution was used as a photometer. It absorbs over much the same spectral region as chloroform, and is decomposed by this light to potassium nitrite with a quantum yield, according to Warburg,[9] varying from 0.17 at 2530 Å. to 0.25 at 2070 Å. Villars[10] has recently investigated the reaction, and finds higher yields than Warburg, but has not gone to as short wave lengths. Consequently, Warburg's figure of 0.25 has been used in calculating the present experiments, with the knowledge that it is probably low. If this is subsequently found to be the case, the results here presented will have to be raised proportionately.

The potassium nitrate was used as recommended by Gillam and Morton[11] as a 0.33 *N* solution buffered with a borate buffer at $P_H$ 9.4, and the decomposition determined iodimetrically by Villars' method, using 0.001 *N* sodium thiosulfate, restandardized daily. It was found best to keep a stream of carbon dioxide bubbling through the solution during the actual titration, since with such very weak thiosulfate, the endpoint was readily affected by air.

Since both chloroform and potassium nitrate absorb over a short range of the spec-

[9] Warburg, *Sitzb. preuss. Akad. Wiss.*, 1228 (1918); *Z. Elektrochem.*, **25**, 223 (1918).

[10] Villars, THIS JOURNAL, **49**, 326 (1927).

[11] Gillam and Morton, *J. Chem. Soc.*, **46**, 415T (1927).

trum only, no filters were used. Few lines in the active region were emitted by the light sources, and filters if available would cut down the intensity objectionably.

The light intensity from the spark varied as much as 100% from one run to another, so that a second reference cell was set opposite to that in the circulatory system, and filled with the potassium nitrate solution. Thus the ratio of the decompositions in the two cells with no chloroform present (averaged over blank runs before and after each experiment) permitted the calculation, from the reaction in the reference cell during an experiment, of the light entering the chloroform, while the photometer cell behind the chloroform recorded directly the light leaving the reaction chamber.

In making a run, chloroform was allowed to enter the carefully evacuated system until the desired pressure was reached, and the apparatus sealed off from the reservoir at a constriction, with the chloroform frozen by carbon dioxide snow. The chloroform was re-evaporated, and streamed through the reaction chamber, then over solid potassium carbonate suspended on glass beads, followed by calcium oxide to remove the carbon dioxide formed in the reaction of the potassium carbonate with the hydrogen chloride produced. The purified gas then passed to the circulating pump, and again to the reaction vessel.

At first a pump with a mercury piston was used, but the mercury was gradually attacked, presumably by unsaturated compounds formed in the reaction, so that it was replaced by an all-glass magnetically operated pump. No difference in the results with the two pumps was observed, nor did variations in pumping velocity appear to affect anything other than the speed with which the window of the reaction vessel was rendered non-transparent.

No attempt was made to remove mercury vapor from the system, and since the chloroform was stored behind a column of mercury, it may be presumed to have been saturated with that substance. It does not seem likely that this could have introduced any errors in the experiments, for the light was not of the type to make a photosensitized reaction at all probable, while the possibility of reactions with mercury playing a part in the secondary reactions seems unlikely when the very low concentration of both mercury vapor and of reaction products is considered.

The amount of decomposition was determined at the end of an exposure by washing out the potassium carbonate tube with water, acidifying and precipitating the chloride as silver chloride.

## Experimental Results

Table I gives the experimental results obtained for chloroform alone under various pressures, and light sources.

In no case were lower yields obtained. In a number of experiments, particularly the early ones, higher yields were found, but these were always erratic, and could not be duplicated. It is believed that they were due either to faulty analysis in the early cases, or to small accidental traces of oxygen, to which the reaction is extraordinarily sensitive. As will be seen, the yield is independent of pressure over the range used, thus implying complete absorption of the light at all times. Likewise, within the limits of accuracy, it made no difference whether the aluminum spark with its active light of wave lengths 1935 Å., 1989 Å. and 2094 Å. was used, or the zinc spark, which contained the three lines, 2025 Å., 2062 Å. and 2100 Å.

**Effect of Temperature.**—Only qualitative measurements on the effect of temperature were made. It was difficult from the experimental stand-

TABLE I

CHLOROFORM RESULTS

| Expt. no. | Press. $CHCl_3$, mm. | Time of exposure, min. | Quanta absorbed, einsteins | Moles of HCl, found | Quantum yield | Light sources |
|---|---|---|---|---|---|---|
| 9 | 101.5 | 31 | $9.00\times10^{-6}$ | $3.42\times10^{-5}$ | 3.8 | Al |
| 10 | 95.0 | 30 | 5.52 | 2.09 | 3.8 | |
| 11 | 97.5 | 90 | 11.6 | 4.18 | 3.6 | |
| 12 | 100.0 | 30 | 6.92 | 2.65 | 3.8 | |
| 15 | 50.0 | 60 | 6.44 | 1.74 | 2.7 | |
| 16 | 46.0 | 60 | 5.64 | 2.30 | 4.1 | |
| 17 | 53.0 | 60 | 6.40 | 3.00 | 4.7 | Zn |
| 18 | 49.0 | 60 | 4.42 | 2.02 | 4.8 | |
| 24 | 52.0 | 60 | 2.42 | 0.84 | 3.5 | |
| 28 | 99.5 | 62 | 3.35 | 1.40 | 4.2 | |
| 29 | 49.0 | 65 | 4.79 | 2.30 | 4.8 | |
| 32 | 52.5 | 64 | 1.64 | 0.63 | 3.8 | |
| 33 | 101.5 | 60 | 2.34 | .84 | 3.7 | |
| 42 | 204.5 | 60 | 2.41 | .98 | 4.1 | |
| | | | | Average | 3.99 | |

point to devise thermostatic control, and not interpose windows diminishing the light intensity. Consequently, the experiments were made in the open air, and the observation made that the heating of the vapor to approximately 35° from the heating effect of the solenoid which worked the glass pump did not give a yield measurably different from that obtained with the mercury pump where no heat was developed.

**Effect of Foreign Gases.**—Table II shows the effect of adding, respectively, hydrogen, nitrogen or oxygen (in one case air) to 100 mm. of chloroform.

The earlier experiments showed an increased yield in the presence of hydrogen, though not as great as with nitrogen. But as greater pains were taken to remove oxygen, the yield with hydrogen dropped to a value indistinguishable from that in its absence. The purification of nitrogen is more difficult, and while it is believed that streaming it over hot freshly reduced copper removed substantially all the oxygen, it might be more nearly correct to say that nitrogen probably increases the yield, while hydrogen definitely is without effect on it. An effect of this kind with nitrogen is known in other chain reactions.

Oxygen, on the other hand, accelerates the reaction enormously, even when present to a very small extent. The last column shows that the accelerating effect of oxygen is roughly proportional to the square of the oxygen pressure. In the presence of air, the yield is less than with an equivalent amount of oxygen, showing that the nitrogen is capable of breaking the chains set up by the oxygen, as well as prolonging the chains set up in pure chloroform. This double effect, while not inconceivable, is certainly rather puzzling, and no explanation is offered.

TABLE II

$CHCl_3 + H_2$

| Expt. | Press. $CHCl_3$, mm. | Press. $H_2$, mm. | Time of exposure, mm. | Quanta absorbed, einsteins | Moles HCl, found | Quantum yield | Light source |
|---|---|---|---|---|---|---|---|
| 37 | 101.0 | 104.5 | 60 | $1.86 \times 10^{-6}$ | $1.67 \times 10^{-5}$ | 9.0 | Zn |
| 40 | 99.0 | 100.5 | 60 | 1.92 | 1.67 | 8.7 | Zn |
| 41 | 100.5 | 51.0 | 60 | 2.97 | 2.23 | 7.5 | Zn |
| 45 | 100.5 | 101.5 | 60 | 4.40 | 1.39 | 3.2 | Zn |
| 49 | 98.0 | 55.0 | 60 | 3.63 | 0.91 | 2.5 | Zn |

$CHCl_3 + N_2$

| | | Press. $N_2$, mm. | | | | | |
|---|---|---|---|---|---|---|---|
| 43 | 99.5 | 101.5 | 60 | $1.78 \times 10^{-6}$ | $3.83 \times 10^{-5}$ | 21.5 | Zn |
| 44 | 100.0 | 54.5 | 60 | 1.16 | 3.00 | 25.8 | Zn |
| 47 | 103.5 | 100.0 | 60 | 1.70 | 4.52 | 26.5 | Zn |
| 48 | 100.0 | 54.0 | 65 | 1.58 | 2.92 | 18.5 | Zn |

$CHCl_3 + O_2$

| | | Press. $O_2$, mm. | | | | | | Quantum yield/$(P_{O_2})^2$ |
|---|---|---|---|---|---|---|---|---|
| 27 | 99.5 | 6.5 | 60 | $1.77 \times 10^{-6}$ | $1.08 \times 10^{-4}$ | 61 | Al | 1.5 |
| 35 | 100.0 | 2.0 | 60 | 4.64 | $4.12 \times 10^{-5}$ | 9 | Zn | 2.3 |
| 38 | 101.0 | 18.0 | 60 | 0.45 | $4.13 \times 10^{-4}$ | 922 | Zn | 2.8 |
| | | Air | | | | | | |
| 26 | 101.0 | 101.0 | 62 | $2.28 \times 10^{-6}$ | $6.60 \times 10^{-4}$ | 289 | Al | |

**Organic Products.**—An attempt was made to study the other products of the reaction by rinsing the reaction vessel with pure chloroform, in which the deposit was soluble, and combining the rinsings from a number of experiments. The total quantity thus obtained was still extremely small, and required treatment by micro-chemical methods, for assistance in which the author is indebted to Dr. Erich Mosettig of the Drug Addiction Laboratory of this University. The product from the chloroform solution was subjected to fractional sublimation, and two fractions were obtained. The one crystallized from petroleum ether, and melted at 120–121° with slight decomposition. The other was an oil, which solidified slowly after some days, and on which no melting point could be taken. The properties of these substances do not agree with those of hexachloroethane, tetrachloroethylene or hexachlorobenzene, the three substances isolated by Löb in the work previously cited on the decomposition at a hot wire, and which might be expected to appear here as well. The quantities were so small that it was not possible to proceed further in the identification.

**Mechanism of the Decomposition.**—A mechanism has been devised for the reaction in the belief that the significant points are best brought out by such a discussion. Unfortunately, the data at hand do not permit of a final decision as to mechanism. The process proposed must, however, involve a primary dissociation of the chloroform molecule by the light absorbed. In the work on alkyl halides cited above, this primary dissocia-

tion has been supposed to be one into a free alkyl radical and a halogen atom. The process may be similar in this case but, due to the large excess energy of the light used, the splitting out of a hydrogen atom is also possible. The fact that no chlorine is found in the exposed vapors does not, as will appear, make its primary production any less likely. One would not expect to find it at the end. Consequently it is assumed that either a hydrogen or a chlorine atom is the primary product of the dissociation.

But whichever is originally produced, it should react on collision with the next chloroform molecule to give a free radical and a hydrogen chloride molecule

$$CHCl_3 + h\nu = CHCl_2 + Cl + (66\text{–}72)\ \text{K. cal., or} \quad (1)$$
$$CHCl_3 + h\nu = CCl_3 + H + (41\text{–}46)\ \text{K. cal.}$$

$$CHCl_3 + Cl = CCl_3 + HCl + 4.6\ \text{K. cal., or} \quad (2)$$
$$CHCl_3 + H = CHCl_2 + HCl + 3.6\ \text{K. cal.}$$

(The values of the linkage energies used are taken from the tabulation of Cronheim and Günther[12] in their discussion of the x-ray decomposition of chloroform.).

The two radicals thus formed are capable of reaction only when activated, since the reactions are slightly endothermic

$$CHCl_2 + CHCl_3 = Cl + C_2H_2Cl_4 - 2\ \text{K. cal.} \quad (3)$$
$$CCl_3 + CHCl_3 = Cl + C_2HCl_5 - 2\ \text{K. cal.} \quad (4)$$

However, the necessary energy should be present in the radicals, for the atomic reactions under (2) proceed with an evolution of energy, part of which should be retained by the radical. If this is the case, the atoms produced by reactions (3) and (4) can react as in (2), and a chain process is established which can account for the production of four molecules of hydrogen chloride per quantum absorbed.

This chain will end when the radical loses the necessary energy by a deactivating collision before reaction, the experiments showing that this event occurs after approximately four molecules of hydrogen chloride have been formed. However, such a deactivating process does not explain the effect of nitrogen in lengthening the chains, as opposed to that of hydrogen.

The accelerating effect of oxygen, on the other hand, is easily accounted for. The reaction of a free radical with an oxygen molecule is exothermic

$$CCl_3 + O_2 = COCl + Cl_2O + 1\ \text{K. cal.} \quad (5)$$
$$CHCl_2 + O_2 = HOCl + COCl + 52\ \text{K. cal.}$$
$$COCl + CHCl_3 = COCl_2 + CHCl_2 + 2\ \text{K. cal.} \quad (6)$$

Other reactions with oxygen are possible, but the above meet the qualifications of producing a large yield of chloride, as shown, and also of causing the liberation of iodine from potassium iodide solution, when the gas ex-

[12] Cronheim and Günther, *Z. physik. Chem.*, **B9**, 201 (1930).

posed in the presence of oxygen is streamed into that solution. This effect was obtained in qualitative experiments with the brass arc.

This qualitative agreement does not, however, explain the dependence of the quantum yield in the presence of oxygen upon the square of the oxygen pressure. The experiments show that the effect is unquestionable, but it has not so far been possible to devise an explanation for it.

Some evidence which helps to establish the chain mechanism proposed may be found from a consideration of the photochlorination of chloroform, investigated in the gas phase by Coehn and Cordes,[13] and in carbon tetrachloride solution by Schwab and Heyde.[14] The former, using light of wave length 4350 Å., find a quantum yield of 1000, while the latter find, even in solution, a yield of from four to fourteen. The writer had attempted to study the gas phase reaction using light of wave length 3650 Å. but after a number of experiments in which no consistency could be obtained between the amount of chlorine used and the amount of hydrogen chloride formed, abandoned the study. The results as obtained, however, were in agreement with the above-mentioned work, for the yield was certainly more than 100.

This reaction is undoubtedly one between chloroform and chlorine atoms, in which the atoms in the chain are most probably regenerated by reaction of the free radicals with a chlorine molecule. This reaction is exothermic, since the linkage energy of the chlorine molecule is only 58.5 K. cal. as opposed to 73 K. cal. of the C–Cl linkage. It then becomes plausible to ascribe the shortness of the chain in the present experiments to the loss of energy necessary for the reactions listed in (3) and (4) since the atomic reactions are shown by the chlorination experiments to be very efficient. Why the necessary energy should be lost when exactly four molecules of hydrogen chloride have been produced is at present not explained.

In that connection it is of interest to recall that Cronheim and Günther[15] in the study of the x-ray decomposition of chloroform also find evidence for a chain reaction long enough to produce approximately four molecules of hydrogen chloride per chain.

## Summary

The decomposition of chloroform in the vapor phase when illuminated with far ultraviolet light has been investigated, with the following results.

1. The decomposition proceeds in a streaming system, giving hydrogen chloride, but not chlorine as the inorganic product.

2. The reaction proceeds as a short chain reaction, yielding four molecules of hydrogen chloride per quantum absorbed.

[13] Coehn and Cordes, *Z. physik. Chem.*, **B9**, 1 (1930).

[14] Schwab and Heyde, *ibid.*, **B8**, 147 (1930).

[15] Cronheim and Günther, Ref. 12; also, *Z. Elektrochem.*, **34**, 616 (1928).

3. The yield is not affected by hydrogen, is probably increased by nitrogen, and very greatly increased by oxygen, in the presence of which, however, the reaction probably proceeds in a different manner.

4. A discussion of the possible mechanism leaves the exact formulation of the reaction unclear, but shows that as far as can at present be established, the results are in accord with other work, and with theoretical considerations.

UNIVERSITY, VIRGINIA

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

# DETERMINATION OF THE FREE ENERGY OF FERROUS HYDROXIDE FROM MEASUREMENTS OF ELECTROMOTIVE FORCE

BY MERLE RANDALL AND MIKKEL FRANDSEN

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The purpose of this investigation was to determine the standard free energy of formation of ferrous hydroxide. This was accomplished by measurements of electromotive force, and the result is compared with others obtained from diverse determinations of the solubility product.

## Apparatus and Materials

Measurements were made on a series of cells of the type

$$Fe(s),\ Fe(OH)_2(s),\ Ba(OH)_2\ 0.05\ M,\ HgO(s),\ Hg(l)$$

in which various samples of iron were used. In addition, a few cells of the type

$$Fe(s),\ Fe(OH)_3(s),\ Ba(OH)_2\ 0.05\ M,\ HgO(s),\ Hg(l)$$

were included, in which only iron deposited by electrolysis upon platinum electrodes was used. The cells were built with special care to exclude oxygen, and placed in an oil thermostat maintained at 25°. The electromotive forces were measured on the potentiometer described by Lewis, Brighton and Sebastian.[1]

**Iron.**—Four different kinds of iron were used, prepared by the following methods.

(1) Electrolytically, by the Fischer–Langbein process.[2] The electrolyte was prepared from C. P. hydrochloric acid, pure iron wire in excess, C. P. calcium chloride and distilled water. The iron was deposited upon bright platinum electrodes, 1.3 by 1.3 cm., and pure iron wire served as anode. The electrolysis was performed at the bottom of a U-tube with square corners which was immersed in an oil-bath maintained at 110°, at which temperature practically no hydrogen[2] is included in the iron depositing on the cathode. In most cases the current density was maintained at 0.15 amp. per sq. cm.

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[1] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2246 (1917).

[2] Allmand and Ellingham, "Applied Electrochemistry," Longmans, Green and Company, New York, **1924**, p. 347.

of that side of the electrode which was facing the anode. It was found, however, that within wide limits the electromotive behavior of this kind of iron is independent of the current density at which the iron is deposited. About 0.25 g. of iron was deposited on each side of the platinum.

In building the half-cell shown on the left side of Fig. 1, the glass rod carrying the electrode was inserted in a rubber stopper, which, after being greased with vaseline, was forced into the cylinder. The cylinder was then clamped upside down, and molten paraffin let in through a small glass tube not shown in the figure. As soon as the paraffin had solidified under the stopper, the cylinder was placed in normal position and a solution of deKhotinsky cement in alcohol was poured on top of the rubber stopper, leaving an air-tight layer after evaporation of the alcohol. The cylinder was then flushed successively with 0.1 M hydrochloric acid, conductivity water, and 0.05 M barium hydroxide. In flushing, pure nitrogen was used each time to force liquid out of the cell. After this treatment the electrode was perfectly bright. As shown in Fig. 1 the two half-cells were connected to an intermediate vessel, which was insulated against atmospheric oxygen in a similar manner. After charging the other half-cell with mercury and mercuric oxide the whole cell with all its connections was filled with 0.05 M barium hydroxide.

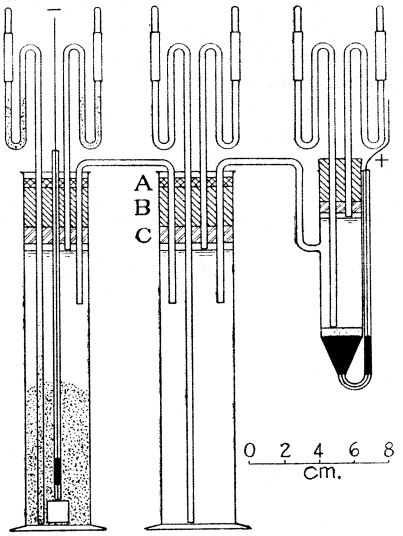


Fig. 1.—Cell containing electrolytic iron, ferrous hydroxide, 0.05 M barium hydroxide, mercuric oxide, mercury. A, de Khotinsky cement; B, rubber stopper; C, paraffin.

By preliminary experiments it had been found that iron is passive in alkaline solution, and that the electromotive force of the cell does not correspond to a reversible reaction under these circumstances. However, passive iron becomes active when charged cathodically with hydrogen.[3] This kind of iron electrodes, as well as those described under (2) and (3), were therefore electrolyzed as cathode, with a platinum electrode, not shown on the figure, as anode, for ten minutes with a current of ten to fourteen milliamperes. As this caused a slight change in the concentration of the barium hydroxide, the half-cell containing iron was again flushed with fresh 0.05 M barium hydroxide. Finally, the iron electrode was completely submerged in a thick suspension of ferrous hydroxide in 0.05 M barium hydroxide. Some of this suspension left in the S-shaped in- and outlets of the cell prevented oxygen from diffusing into the cell through these.

(2) By reduction of pure iron oxide with hydrogen, according to the method of Richards and Behr.[4] The reduction was carried out at a temperature of 800 to 850°. The hydrogen required for the reduction was prepared and carefully purified in the cryogenic laboratory; no impurities were deposited when it was passed through a liquid air trap. The resulting samples of iron were stored in glass tubes filled with pure hydrogen.

The half-cell used for this kind of iron was similar to the one shown on the right side of Fig. 1. The platinum lead at the bottom, however, was curled up into a ring, about one cm. in diameter, placed horizontally a little above the bottom. Several pieces of

[3] Ref. 2, p. 259.

[4] Richards and Behr, Carnegie Inst. Pub. No. 61 (1906).

iron were thrown down upon this ring, whereby a large surface of iron in good contact with the platinum wire was obtained. When connection had been made to the half-cell containing mercury, the iron was completely submerged in a thick suspension of ferrous hydroxide in 0.05 M barium hydroxide.

(3) We are indebted to the firm of Pike and West of San Francisco for a sample of commercial electrolytic iron from their experimental unit. They reported the following impurities in the sample: carbon 0.0075%, sulfur 0.0075%, copper 0.022%.

This iron had not been prepared by Fischer's process. It contained a small amount of hydrogen, which made it somewhat brittle. All traces of rust were removed from it by filing. Some coarse filings and a few small pieces were then produced from it with a hard clean file, and placed in a half-cell similar to the one used for the iron produced by reduction of iron oxide.

(4) A small recently charged Edison cell was flushed and filled with conductivity water, allowed to stand overnight, and again emptied and filled. This was repeated several times, until the original electrolyte had been thoroughly removed. Pure nitrogen was used for displacing the liquid. The cell was then repeatedly flushed and filled with 0.05 M barium hydroxide, a rubber stopper with glass tubing was placed in its neck, and connection was made in the usual manner to a half-cell containing $Ba(OH)_2$ 0.05 M, HgO(s), Hg(l).

**Ferrous Hydroxide.**—About 8 g. of pure iron wire, 99.8% Fe, was placed in the 750-cc. tube, shown in Fig. 2, and the air in this displaced by pure hydrogen. Twelve cc. of concentrated hydrochloric acid, corresponding to 4 g. of iron, was diluted with an equal volume of water and charged into the tube, and the mixture was heated. The excess of iron prevented the formation of ferric ion. When the acid had been used up, 200 cc. of distilled water from which dissolved gases had been expelled by boiling was added through C and immediately followed by 200 cc. of a solution of barium hydroxide from which dissolved oxygen had been similarly removed. This solution contained enough barium hydroxide to precipitate the iron and make the mixture about 0.05 M with respect to barium hydroxide. After settling overnight about four-fifths of the solution was forced out through A with pure hydrogen coming in through B; the tube was filled again with 0.05 M barium hydroxide, and the contents thoroughly mixed. By repeating this decantation six to seven times, a thick suspension of solid ferrous hydroxide in 0.05 M barium hydroxide was obtained in the lower part of the tube.

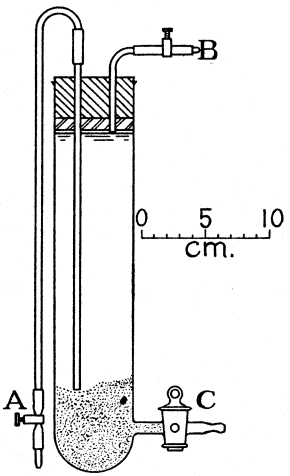

Fig. 2.—Tube for preparation of ferrous hydroxide.

**Ferric Hydroxide.**—In the tube shown in Fig. 2 a concentrated solution of ferric chloride was boiled with a little concentrated nitric acid in order to oxidize every trace of ferrous ion to ferric ion, diluted with freshly boiled distilled water, precipitated and repeatedly decanted with barium hydroxide, in order to produce a thick suspension of solid ferric hydroxide in 0.05 M barium hydroxide.

**Barium Hydroxide.**—As a solution of barium hydroxide contains no carbonate it was used in preference to sodium or potassium hydroxide. One single batch of 0.05 M barium hydroxide,[5] large enough for the entire investigation, was prepared at the

[5] All concentrations are expressed in moles per 1000 g. of water. Vacuum corrections have been applied to all weights.

start. Early in these experiments it was found necessary to remove completely dissolved oxygen. This was done by boiling the solution for half an hour in a flask fitted with a reflux condenser. In order to remove impurities such as lead and arsenic some iron wire was added before boiling. The air above the boiling solution was displaced with pure hydrogen.

**Mercuric Oxide.**—Mercuric oxide was prepared by heating c. p. $HgNO_3 \cdot 2H_2O$ in an electric furnace to about 500° with stirring. The residue was ground, washed with conductivity water, and dried at 105°. Ordinarily, duplicates of electrodes in which this oxide was used would differ only by 0.0005 volt or less. In the final experiments the mercuric oxide electrodes were checked against a hydrogen electrode.

**Mercury.**—The mercury was refined by washing with dilute nitric acid in the usual manner, followed by distillation in a current of air.

**Nitrogen.**—Pure nitrogen was prepared whenever needed by gentle heating of a solution of 1 part of sodium nitrite, 1.5 parts of ammonium sulfate, and 1 part of potassium chromate in 4 parts of water. The gas was washed with a mixture of 1 volume of concentrated sulfuric acid and 5 volumes of saturated potassium dichromate solution.[6]

## Data and Discussion

The variation of the electromotive forces of the various cells with time is shown graphically in Fig. 3. To avoid excessive overlapping all curves but $a_1$ have been plotted at an arbitrary distance from the vertical axis.

It will be noticed that the electromotive force is increasing from the start in all cells. This is ascribed to the fact that all iron electrodes, as mentioned previously, were activated by cathodic charging with hydrogen. Probably the charge of hydrogen makes them behave in part as hydrogen electrodes. It is thought that the two half-cell reactions

$$H_2(g) + 2OH^- = 2H_2O(l) + 2E^- \quad (1)$$

and

$$Fe(s) + 2OH^- = Fe(OH)_2(s) + 2E^- \quad (2)$$

tend to occur simultaneously at the iron electrode. By checking the mercury half-cell against a hydrogen electrode, the electromotive force of the cell

$$Pt, H_2(g), Ba(OH)_2\ 0.05\ M, HgO(s), Hg(l)$$

was found to be 0.9266 volt, in close agreement with the values given by Brönsted and Ming Chow for similar cells.[7] This is, therefore, the potential corresponding to reaction (1). In course of time the charge of hydrogen is lost by diffusion, and the electromotive force of the cell approaches the value corresponding to reaction (2). The fluctuations of the cells $a_1$, $a_2$ and $a_3$ indicate other disturbing influences in addition to hydrogen.

When it was realized that a relatively long time would be required for the establishment of equilibrium in the cells, the measurements were discon-

[6] See Gmelin-Kraut, "Handbuch der anorganischen Chemie," Heidelberg, 1907, Vol. I, 1, 171.

[7] Brönsted, *Z. physik. Chem.*, **65**, 84, 744 (1909); Ming Chow, THIS JOURNAL, **42**, 488 (1920).

tinued for more than one year. At the end of this period the electromotive force of Cell $a_1$ proved to be the same as before, a value which both Cell $a_2$ and Cell $a_3$ by that time had very nearly attained also. In Cells $b_1$, $b_2$ and c the contact between the iron and the platinum wire had been destroyed, probably by an insulating coating of ferrous hydroxide formed on the iron during the prolonged submersion.

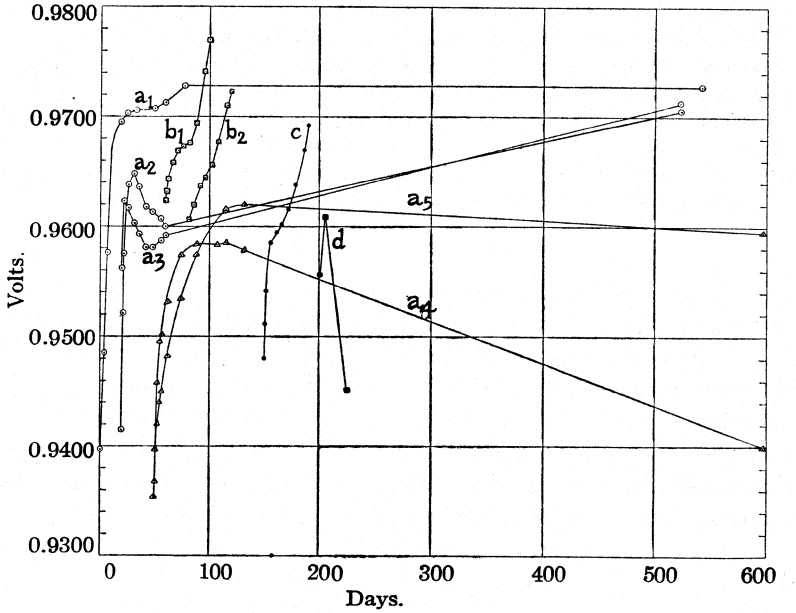


Fig. 3.—Variation of the electromotive force of cells of the type Fe(s), $Fe(OH)_2$(s), $Ba(OH)_2$ 0.05 M, HgO(s), Hg(l) with time. Cells $a_1$ to $a_5$ contained electrolytic iron; Cells $b_1$ and b iron produced by reduction; Cell c, commercial electrolytic iron; Cell d, iron from an Edison cell. Cells $a_4$ and $a_5$ contained ferric hydroxide instead of ferrous hydroxide.

The electromotive forces of the cells containing iron produced by reduction of iron oxide, namely, Cells $b_1$ and $b_2$, seem to approach a higher value than the others. This is in accord with observations made by Hampton,[8] and by Richards and Behr,[4] who state that the higher escaping tendency of this kind of iron probably is due to the presence of very finely divided particles of iron.

From Cells $a_4$ and $a_5$ it is seen that the presence of ferric hydroxide around the iron electrode lowers the electromotive force of the cell, and prevents it from assuming a constant, reproducible value. A similar phenomenon is observed in Cell d into which air was admitted accidentally when its electromotive force had reached a value of 0.9609 volt. The ensuing decrease

[8] Hampton, *J. Phys. Chem.*, **30**, 980 (1926).

of the electromotive force was probably due to formation of ferric hydroxide around the iron.

On the whole, the agreement between the various ferrous hydroxide cells containing different kinds of iron is not bad when the sluggish nature of these cells is taken into consideration. The fact that Cells $a_1$, $a_2$ and $a_3$ in the end show very nearly the same electromotive force is very gratifying, and we feel justified in selecting

$$E_{298} = 0.973 \pm 0.005 \text{ volt}$$

for the final equilibrium potential of the ferrous hydroxide cells.

## Calculations

From the preceding measurements we find for the cell reaction

$$\text{Fe(s)} + \text{HgO(s)} + \text{H}_2\text{O(l)} = \text{Hg(l)} + \text{Fe(OH)}_2\text{(s)}$$
$$E_{298} = 0.973 \pm 0.005 \text{ volt}; \quad \Delta F^\circ_{298} = -44{,}900 \pm 230 \text{ cal.} \qquad (3)$$

From the tables of free energy[9] we obtain

$$\text{H}_2\text{(g)} + {}^1/_2\text{O}_2\text{(g)} = \text{H}_2\text{O(l)}; \quad \Delta F^\circ_{298} = -56{,}560 \text{ cal.} \qquad (4)$$
$$\text{Hg(l)} + {}^1/_2\text{O}_2\text{(g)} = \text{HgO(s)}; \quad \Delta F^\circ_{398} = -13{,}940 \text{ cal.} \qquad (5)$$

Adding Equations (3), (4) and (5) we obtain

$$\text{Fe(s)} + \text{O}_2\text{(g)} + \text{H}_2\text{(g)} = \text{Fe(OH)}_2\text{(s)}; \quad \Delta F^\circ_{298} = -115{,}400 \text{ cal.} \qquad (6)$$

For comparison the free energy of formation of ferrous hydroxide may be calculated from data obtained by other methods. We have for the reaction

$$\text{Fe}^{++} + 2\text{OH}^- = \text{Fe(OH)}_2\text{(s)}; \quad \Delta F^\circ = -RT \ln K \qquad (7)$$

where $K$ is the solubility product of ferrous hydroxide. From the free energy table we obtain

$$\text{H}_2\text{(g)} + \text{O}_2\text{(g)} + 2\text{E}^- = 2\text{OH}^-; \quad \Delta F^\circ = -74{,}910 \text{ cal.} \qquad (8)$$

and in the following paper we shall find

$$\text{Fe(s)} = \text{Fe}^{++} + 2\text{E}^-; \quad \Delta F^\circ = -20{,}310 \text{ cal.} \qquad (9)$$

By addition of Equations (7), (8) and (9) we then have

$$\text{Fe(s)} + \text{O}_2\text{(g)} + \text{H}_2\text{(g)} = \text{Fe(OH)}_2\text{(s)}; \quad \Delta F^\circ = -95{,}220 - RT \ln K \qquad (10)$$

Diverse values of the solubility product $K$, determined in various ways, are given in Table I together with corresponding values of the free energy calculated by means of Equation (10).

It is seen that our value, 115,400 calories, is in good agreement with the average result of these determinations.

Calculating backwards from our result we find for the solubility product of ferrous hydroxide, $K = 1.45 \times 10^{-15}$.

In conclusion, we shall use our determination to calculate whether the reaction

$$\text{Fe(s)} + 2\text{H}_2\text{O(l)} = \text{Fe(OH)}_2\text{(s)} + \text{H}_{2(1 \text{ atm.})}$$

[9] "International Critical Tables," Vol. VII, 1930, pp. 232, 258.

TABLE I

CALCULATION OF THE FREE ENERGY OF FORMATION OF FERROUS HYDROXIDE FROM ITS SOLUBILITY PRODUCT

| Solubility product | Method of determining solubility product | Authority | $-\Delta F°$, calories |
|---|---|---|---|
| $1.64 \times 10^{-14}$ | Calculated from Bodländer's formula, *Z. physik. Chem.*, **27**, 56 (1898) | (1) | 114,000 |
| $8.7 \times 10^{-14}$ | From activities of the ions in 20% KOH solution; ($Fe^{++}$) from e. m. f. measurements | (2) | 113,000 |
| $9.84 \times 10^{-15}$ | Conductivity measurements | (3) | 114,300 |
| $7.93 \times 10^{-15}$ | $P_H$ measurements | (4) | 114,500 |
| $3.2 \times 10^{-14}$ | $P_H$ measurements | (5) | 113,600 |
| $1.6 \times 10^{-19}$ | Calculated from $P_H$ measurements of Britton, *J. Chem. Soc.*, **127**, 2118 (1925) | (6) | 120,900 |
| $4.8 \times 10^{-16}$ | $P_H$ measurements | (7) | 116,100 |
| | | Average | 115,200 |

(1) E. Müller, *Z. Electrochem.*, **14**, 77 (1908). (2) P. Krassa, *ibid.*, **15**, 490 (1909). (3) A. B. Lamb, THIS JOURNAL, **32**, 1214 (1910). (4) Shipley and McHaffie, *Can. Chem. Met.*, **8**, 121 (1924). (5) Whitman, Russell and Davis, THIS JOURNAL, **47**, 70 (1925). (6) W. J. Sweeney, *Trans. Am. Electrochem. Soc.*, **53**, 317 (1928). (7) L. W. Elder, *ibid.*, **57**, 383 (1930).

according to which iron is corroded by pure water, is thermodynamically possible. For the free energy of this reaction we find

$$\Delta F°_{298} = 2 \times 56{,}560 - 115{,}400 = -2280 \text{ cal.}$$

Hence it is seen that iron and pure water actually have a small tendency to form solid ferrous hydroxide and free hydrogen.

## Summary

1. The electromotive force of the cell

$$Fe(s), Fe(OH)_2(s), Ba(OH)_2\ 0.05\ M, HgO(s), Hg(l)$$

in which pure iron prepared in different ways was employed, was found to be 0.973 ± 0.005 volt at 25°.

2. From this determination the standard free energy of formation of ferrous hydroxide is calculated to be −115,400 calories, in good agreement with the average of values calculated from diverse determinations of the solubility product.

3. Hence we find

$$Fe(s) + 2H_2O(l) = Fe(OH)_2(s) + H_{2(1\ atm.)};\ \Delta F°_{298} = -2280 \text{ cal.}$$

which shows that iron and pure water have a small tendency to form ferrous hydroxide and free hydrogen.

BERKELEY, CALIFORNIA

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

# THE STANDARD ELECTRODE POTENTIAL OF IRON AND THE ACTIVITY COEFFICIENT OF FERROUS CHLORIDE

BY MERLE RANDALL AND MIKKEL FRANDSEN

RECEIVED JULY 13, 1931 PUBLISHED JANUARY 7, 1932

Richards and Behr[1] made a comprehensive study of the difference in potential of various kinds of iron, differing in mode of preparation and in mechanical and thermal treatment. Differences of about three centivolts were encountered. They considered pure iron, produced by reduction of iron oxide with hydrogen and subsequently fused in vacuum, as the normal or standard form of iron; with this form they found 0.76 volt for the electromotive force of the cell

$$Fe(s), FeSO_4\ 0.5\ M, KCl\ 0.1\ M, HgCl(s), Hg(l)$$

Unfortunately, the unknown activity of the ferrous ion in this concentrated solution and the unknown liquid potential involved make it impossible to calculate the standard electrode potential from this determination.

Hampton[2] used pure iron produced by reduction of iron oxide with hydrogen at about 800° as the standard form of iron, and avoided liquid potentials using the cell

$$Fe(s), FeCl_2\ 0.1\ M, HgCl(s), Hg(l)$$

Assuming the activity of ferrous chloride to be the same as that of barium chloride, he found 0.4413 volt for the standard electrode potential of iron.

In a recent determination of the free energy of ferrous hydroxide[3] we attempted to use Hampton's standard form of iron in some alkaline cells, but did not succeed because the contact between the iron and the wire at the bottom of the cells was destroyed in a certain length of time. This difficulty was avoided by using electrolytic iron deposited upon platinum electrodes, with which satisfactory measurements were obtained. In the ensuing calculations, however, we had to use a value for the free energy of formation of the ferrous ion, and it became necessary to find out whether Hampton's value would apply to our electrolytic iron. We decided, therefore, to measure the potential of both kinds of iron in cells of the type used by him. In addition, we used a value for the activity coefficient of ferrous chloride calculated from various data given in the literature.

## Apparatus and Materials

As ferrous chloride is a strong reducing agent, it is necessary to take special precautions to avoid oxidation in the cells. A cell used for iron prepared by reduction of the oxide is shown in Fig. 1. It will be noticed

[1] Richards and Behr, Carnegie Inst. Pub. No. 61 (1906).

[2] Hampton, *J. Phys. Chem.*, **30**, 980 (1926).

[3] Randall and Frandsen, THIS JOURNAL, **54**, 40 (1932).

that the two half-cells are closed glass vessels. The S-shaped in- and outlets permit flushing and when left filled with the solution of ferrous chloride they prevent atmospheric oxygen from penetrating into the cell. The iron in the left half-cell was slipped in through the side tube before this was bent into shape.

The half-cells employed for electrolytic iron were similar to that described in our article on ferrous hydroxide.

**Iron.**—The preparation of both kinds of iron was described in the previous paper. After the electrolytic iron had been placed in its half-cell, adhering layers from the bath were removed by flushing with dilute hydrochloric acid and 0.1 *M* ferrous chloride. The iron produced by reduction was placed in the cells without ever coming in contact with air and was first submerged in the solution of ferrous chloride without preceding flushing with acid. Later, however, some samples of this iron were treated with acid as described in the following.

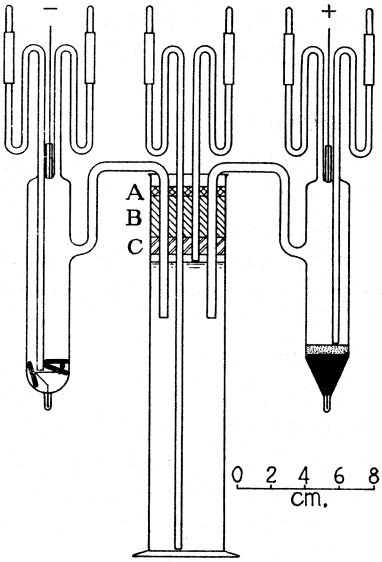


Fig. 1.—Cell containing iron, ferrous chloride 0.1 *M*, calomel, mercury, protected against atmospheric oxygen: A, de Khotinsky cement; B, rubber stopper; C, paraffin.

**Ferrous Chloride Solution.**—A large amount of 0.2 *M* hydrochloric acid was first made by mixing correct weights of constant boiling hydrochloric acid and conductivity water according to the method of Hulett,[4] allowance being made for the small amount of water that later escapes with the hydrogen. This solution was then allowed to react with an excess of pure iron wire in an apparatus similar to that of Richards and Behr.[1] A layer of paraffin 1 cm. thick was cast under the stopper, which was also heavily coated with paraffin on the outside to keep out oxygen.

**Calomel.**—An excess of pure mercury was heated with 25 cc. of 3 *N* nitric acid to 50–60° for half an hour under frequent shaking, the mixture placed on a shaking machine for one hour, then poured into about twenty volumes of conductivity water, and precipitated with 1 *N* hydrochloric acid. The precipitate was washed repeatedly by decantation with conductivity water, and run into a 250-cc. bottle, with an inlet tube at the top and an outlet tube reaching the bottom, and containing pure hydrogen and a little pure mercury. After settling, the main part of the water was forced out with pure hydrogen and replaced with 0.1 *M* ferrous chloride; the bottle was rotated overnight, and the solution was decanted after settling. This was repeated about six times, whereby a suspension of calomel in 0.1 *M* ferrous chloride was obtained, from which the calomel cells containing pure mercury and hydrogen were charged. Half-cells prepared in this manner agreed to 0.00005 volt, and two months later with freshly prepared cells.

**Mercury.**—The mercury was refined by washing with dilute nitric acid in the usual manner, followed by distillation in a current of air.

[4] Hulett, THIS JOURNAL, **31**, 390 (1909).

The cells were placed in an oil thermostat maintained at 25°, and their electromotive force was measured on the potentiometer described by Lewis, Brighton and Sebastian.[5] To avoid erratic results it was found necessary to shake the half-cells containing iron by gentle tapping previous to each measurement.

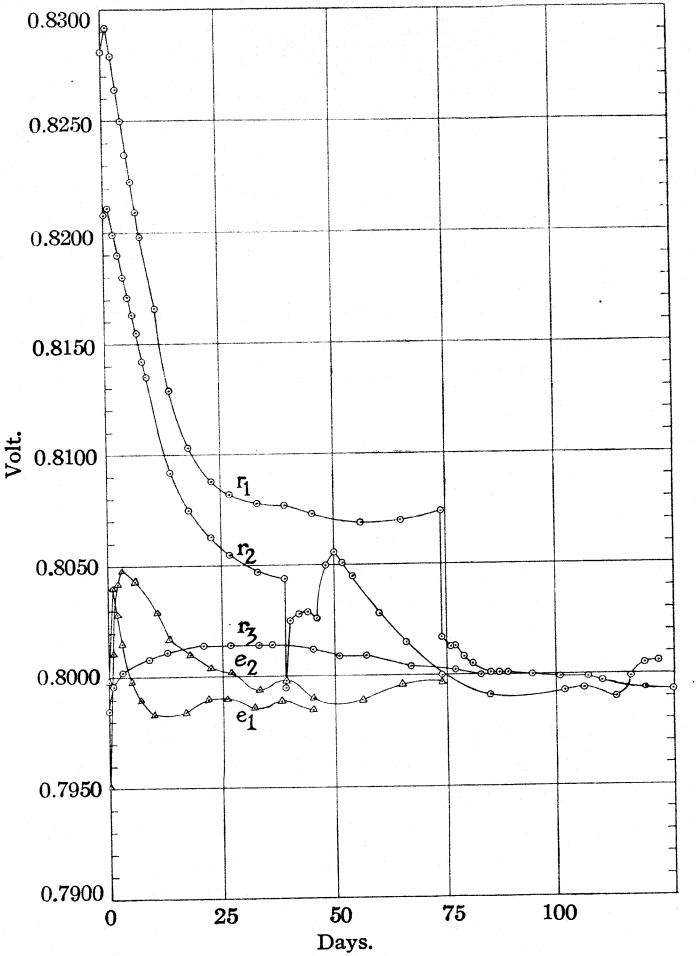


Fig. 2.—Variation of the electromotive force of cells of the type Fe(s), $FeCl_2$ 0.1 *M*, HgCl(s), Hg(l) with time. Cells $r_1$, $r_2$ and $r_3$ contained iron produced by reduction of iron oxide; Cells $e_1$ and $e_2$ contained electrolytic iron.

## Data and Discussion

In Fig. 2 the electromotive force of various cells is shown plotted against time. It is seen that the electromotive force in all cases changes considerably during the first two weeks.

[5] Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2246 (1917).

It has often been observed that the electromotive behavior of the electrolytic iron within wide limits is independent of the current density at which the iron has been deposited. This is demonstrated again by Cells $e_1$ and $e_2$, in which the samples of iron were deposited at current densities of 1.5 and 0.15 amp./sq. cm., respectively.

Richards and Behr observed that the potential of the iron produced by reduction increased with decreasing temperature of the reduction, and ascribed this to the fact that iron produced at lower temperatures is more finely divided. Their observation is confirmed by the potentials of Cells $r_1$, $r_2$ and $r_3$, the samples of iron in which were produced at 770, 800 and 850°, respectively. Besides the temperature the rate of reduction also influences the state of subdivision of the iron, the subdivision of which decreases with increasing rate of reduction.

The iron in Cell $r_3$ was produced in a rapid current of hydrogen, and consisted of well-sintered pieces which did not seem to contain any fine particles. The electromotive force of this cell is, therefore, much closer to that of electrolytic iron than those of the other cells containing iron produced by reduction.

The continued decrease in the electromotive force of Cells $r_1$ and $r_2$ is undoubtedly due to a slow disappearance of the finer particles of iron, which have a higher escaping tendency than the bulk of the iron. To accelerate this process the iron in these two cells was treated after 74 and 39 days, respectively, with 0.2 *M* hydrochloric acid, and then flushed with and again submerged in 0.1 *M* ferrous chloride solution. It is seen from Fig. 2 that after this treatment the electromotive force of these cells became finally almost identical with that of those containing electrolytic iron.

**Equilibrium Potentials.**—From the curves in Fig. 2 we find for the equilibrium potentials of Cells $e_1$ and $e_2$ the values 0.7987 and 0.7994 volt, respectively, from which the average value 0.7990 volt is obtained for the cells containing electrolytic iron. Similarly, we find 0.8000, 0.7992 and 0.8014 volt for Cells $r_1$, $r_2$ and $r_3$, respectively, from which the average value 0.8002 volt is found for the equilibrium potential of the cells containing iron produced by reduction. For both kinds of iron we shall then take $\mathbf{E} = 0.7996 \pm 0.0010$ volt. The close agreement of the equilibrium potential of cells containing either kind of iron with this value may be taken as strong evidence of its correctness.

## The Activity Coefficient of Ferrous Chloride

The activity coefficient of ferrous chloride was calculated by the usual procedures[6] from various data given in the literature. The freezing point data of Biltz and Meyer[7] were the most valuable source, although other

[6] Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

[7] Biltz and Meyer, *Z. physik. Chem.*, **40**, 185 (1902).

measurements[8] also were considered. As usual the heat of dilution was neglected in the calculations. A plot of log $\gamma$ against the square root of the ionic strength, $\mu^{1/2}$, made it possible to draw a curve representing the average of the various results. From this curve the values given in Table I were obtained.

TABLE I

ACTIVITY COEFFICIENT OF FERROUS CHLORIDE AT THE FREEZING POINT

| Molality | Log $\gamma$ | Molality | Log $\gamma$ |
|---|---|---|---|
| 0.001 | −0.048 | 0.05 | −0.205 |
| .002 | − .065 | .1 | − .236 |
| .005 | − .095 | .2 | − .252 |
| .01 | − .124 | .5 | − .234 |
| .02 | − .157 | 1.0 | − .175 |

Although the vapor pressure measurements of Tammann indicate that the activity coefficient of ferrous chloride decreases slightly with increasing temperature, it will cause no appreciable errors to use the values in Table I at 25° without the application of any temperature correction.

## Discussion of Hampton's Results

In spite of the fact that our cell diagrammatically is identical with Hampton's, our determination of its equilibrium potential, 0.7996 volt, is considerably lower than his value, 0.8088 volt. From a careful study of his work,[2,9] we are led to believe that in his choice of the equilibrium potential he was misled by the tendency of finely divided iron to give too high values. Our reasons for this conclusion are the following.

(1) Treatment with acid reduces the activity of Hampton's "finely divided iron" to our value. Our Cells $r_1$ and $r_2$ were prepared essentially in the same manner as Cells 6 and 7 of Hampton's publication, and, as shown on Fig. 2, the electromotive force of Cell $r_1$ was for a long time nearly constant at about 0.8072 volt, a value which differs only little from the apparent equilibrium potential, 0.8088 of Hampton's Cell 7. The potential 0.8072 volt, however, does not correspond to a true equilibrium because Cells $r_1$ and $r_2$ after treatment of the iron with acid, which accelerates the removal of finer particles of iron, attain a nearly constant electromotive force of approximately the same value as shown by Cells $e_1$ and $e_2$, which contained compact electrolytic iron.

(2) Prolonged exposure to solutions of ferrous chloride makes the activity of Hampton's "finely divided iron" approach our value. Some data from which this may be shown are given in Table II.

[8] (a) Goldschmidt and Syngros, *Z. anorg. Chem.*, **5**, 129 (1894); (b) Peters, *Z. physik. Chem.*, **26**, 223 (1898); (c) Vapor pressure measurements, Tammann, *Mem. Acad. Pet.*, [7] **35**, No. 99 (1887).

[9] Hampton, Manuscript Thesis, University of California, Berkeley, California, 1921.

TABLE II

Fe(s), $FeCl_2$(aq.), HgCl(s), Hg(l) AT 25°

| Cell | $m$($FeCl_2$) | E | $\mu^{1/2}$ | Log $\gamma$ + const. |
|---|---|---|---|---|
| Hampton's Thesis No. 33 | 0.5 | 0.7474 | ... | ..... |
| Hampton's Thesis No. 33 | 2.245 | .6592 | ... | ..... |
| Hampton's Thesis No. 33 | 0.1 | .8000 | 0.5477 | −8.2173 |
| Hampton's Publication No. 5 | 0.1 | .8087 | .5477 | −8.3154 |
| Hampton's Publication No. 5 | .0865 | .8136 | .5095 | −8.3077 |
| Hampton's Publication No. 5 | .050 | .8278 | .3873 | −8.2297 |
| Hampton's Publication No. 5 | .0095 | .8826 | .1688 | −8.1260 |
| Hampton's Publication No. 7 | .1 | .8088 | .5477 | −8.3154 |
| Hampton's Publication No. 7 | .01 | .8790 | .1732 | −8.1077 |
| Randall and Frandsen | .1 | .7996 | .5477 | −8.2128 |

In each cell the iron was successively left in contact with various solutions of ferrous chloride, the molalities of which are given in the second column in the order in which they were applied, until the electromotive force had become approximately constant. Values of the electromotive force, **E**, and the square root of the ionic strength, $\mu^{1/2}$, are included in the table. The values of log $\gamma$ + constant have been calculated by the equation[10]

$$\log \gamma + \text{constant} = -\frac{\mathbf{E}}{0.088725} - \log m_{\pm}$$

in which $m_{\pm}$ is the stoichiometric mean molality. The constant is equal to $-\mathbf{E}^{\circ}_{298}/0.088725$, from which $\mathbf{E}^{\circ}_{298}$, the electromotive force of the cell when the ions of the solute are at unit activity, may be found as soon as the value of the constant has been determined.

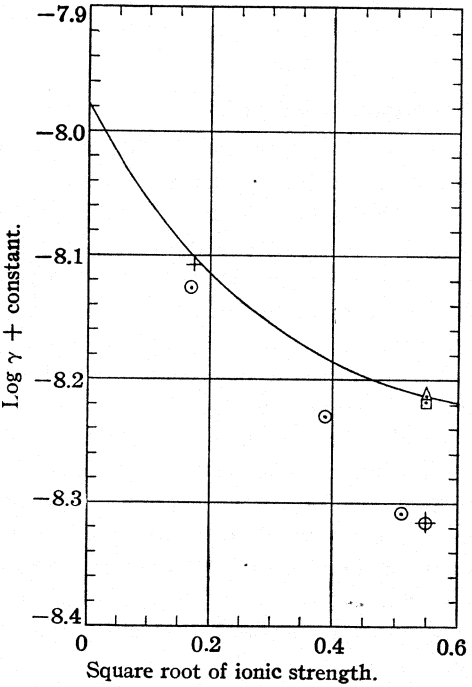


Fig. 3.—Activity coefficient function of ferrous chloride. Solid curve obtained mainly from freezing-point data: ⊡, Hampton Cell 33; ⊙, Hampton Cell 5; +, Hampton Cell 7; △, Randall and Frandsen.

The figures in the last column of Table II are shown plotted against the square root of the ionic strength in Fig. 3. Superimposed upon this plot is shown the curve from the previously mentioned plot of log $\gamma$ against the square

[10] Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

root of the ionic strength, which has been drawn, parallel to its original position, through the point corresponding to $\mathbf{E} = 0.7996$ for 0.1 $M$ ferrous chloride. As the measurements in the more dilute solutions were made last, it is seen that the longer Hampton's iron in each case had been in contact with solutions of ferrous chloride, the closer is the agreement between his determinations and ours. The reason for this is undoubtedly the progressive elimination of very fine particles of iron. Hampton's Cell No. 33 is in agreement with ours because its iron first was treated with other solutions of ferrous chloride as shown in Table II.

(3) Hampton's measurements of the equilibrium

$$Fe(s) + 2TlCl(s) = Fe^{++} + 2Cl^- + 2Tl(s)$$

indicate that his value for the electromotive force is too high. The data in Tables V and VI of his publication give evidence that his approach to the equilibrium from the left was much closer than that from the right. Nevertheless, his value for the electromotive force agrees better with the result of his approach to the equilibrium from the right. In the following calculations it will be shown that our value for the electromotive force nearly coincides with the result of his approach to the equilibrium from the left.

## Calculation of the Standard Electrode Potential

From the intercept of the curve in Fig. 3 on the vertical axis the value of the constant is found to be $-7.977$. Substituting this value in the equation

$$\text{Constant} = -\frac{\mathbf{E}^\circ_{298}}{0.088725} \qquad (1)$$

we find the electromotive force at unit activities $\mathbf{E}^\circ_{298}$, for the cell reaction $Fe(s) + 2HgCl(s) = Fe^{++} + 2Cl^- + 2Hg(l)$; $\mathbf{E}^\circ_{298} = 0.7078$ v.; $\Delta F^\circ_{298} = -32{,}660$ cal. (2)

whence with the value of the potential of the hydrogen–calomel cell obtained by Randall and Young[11]

$$Fe(s) = Fe^{++} + 2E^-; \quad \mathbf{E}^\circ_{298} = 0.4402 \text{ v.}; \quad \Delta F^\circ_{298} = -20{,}310 \text{ cal.} \qquad (3)$$

From Hampton's measurement of the equilibrium approached by the action of iron upon thallous chloride at 25°, $m(Fe^{++}) = 0.0453$, $m(Tl^+) = 0.0042$, $m(Cl^-) = 0.0948$, whence $\log m_\pm = -1.1301$, and $\mu^{1/2} = 0.3743$. Assuming the principle of the ionic strength for the equilibrium mixture, we find from Table I $\log \gamma = -0.2020$; whence $\log a_2 = -3.9963$, and

$$Fe(s) + 2TlCl(s) = Fe^{++} + 2Cl^- + 2Tl(s); \quad \Delta F^\circ_{298} = 5455 \text{ cal.} \qquad (4)$$

With the accurate measurements of Gerke[12]

$$Tl(s) + AgCl(s) = TlCl(s) + Ag(s); \quad \mathbf{E}^\circ_{298} = 0.7790; \quad \Delta F^\circ_{298} = -17{,}975 \text{ cal.} \qquad (5)$$

$$Ag(s) + {}^1/_2Cl_2(g) = AgCl(s); \quad \Delta F^\circ_{298} = -26{,}220 \text{ cal.} \qquad (6)$$

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

[12] Gerke, *ibid.*, **44**, 1684 (1922).

and the preliminary revised value of the free energy of formation of chloride ion (−31,345), we find

$$Fe(s) = Fe^{++} + 2E^{-};\ E^{\circ}_{298} = 0.4387\ v.;\ \Delta F^{\circ}_{298} = -20{,}245\ cal. \qquad (7)$$

In making these measurements Hampton used powdered reduced iron. The treatment with thallous chloride undoubtedly had the same effect as our treatment with hydrochloric acid of first removing the finer particles of iron; the residual iron might, therefore, be expected to give identical results in the two cases. The small difference between the values in Equations 3 and 7 is explained by the fact that complete equilibrium hardly was attained in Hampton's experiments. The measurements of Hampton in which the equilibrium was approached from the action of ferrous chloride upon thallium do not agree with these measurements, but the reaction is very slow and undoubtedly equilibrium was not attained.

## Summary

1. Iron prepared in pure form by electrolysis is shown to have the same potential as pure iron produced by reduction of iron oxide, in ferrous chloride solution.

2. The standard single potential of iron at 25° is found to be 0.4402 volt, and the free energy of formation of ferrous ion to be −20,310 calories.

3. The new potential is shown to agree with the equilibrium experiments of Hampton.

4. A table of values of the activity coefficient of ferrous chloride at the freezing point has been calculated.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

# THE HEATS OF "ADSORPTION" OF OXYGEN ON NICKEL AND COPPER CATALYSTS

BY W. WALKER RUSSELL AND OSBORNE C. BACON[1]

RECEIVED JULY 20, 1931 PUBLISHED JANUARY 7, 1932

It is well known that oxygen has no action on nickel or copper[2] in the massive state at ordinary temperatures. When these metals are sufficiently finely divided to be catalytically active, however, they do take up oxygen readily and may even become pyrophoric.[3] Oxygen may also serve as a poison[4] for the catalytic activity of nickel and copper. A study of the action of oxygen on such surfaces might, therefore, be expected to

[1] From a thesis submitted in May, 1931, by Osborne C. Bacon to the Graduate School in partial fulfilment of the requirements for the degree of Master of Science.

[2] Dunn, *Proc. Roy. Soc.* (London), **A111**, 210 (1926).

[3] Tammann and Nikitin, *Z. anorg. allgem. Chem.*, **135**, 201 (1924).

[4] Benton and Emmett, THIS JOURNAL, **48**, 637 (1926); Pease and Taylor, *ibid.*, **44**, 1637 (1922).

give information regarding their nature and function as catalysts. Especially surfaces produced by the removal of oxygen atoms, *e. g.*, low temperature reduction of oxides, might be expected again to take up oxygen with characteristic effects since the activity of such surfaces must be, in part at least, dependent upon some persistence of the metal oxide lattice. Because of such considerations, it was deemed of interest to investigate the behavior of oxygen toward active nickel and copper surfaces and to this end measurements have been made of the magnitudes of the heats of oxygen adsorption[5] at 0°. In certain cases measurements of the catalytic activity of the same surfaces at 0° have also been carried out.

## Apparatus and Experimental Method

**Apparatus.**—The apparatus consisted essentially of a water jacketed, compensated gas buret, a closed manometer, a Toepler pump and a catalyst bulb. These units were all sealed together to make an all-glass apparatus with suitable stopcocks and connections provided. All of the measuring apparatus was carefully calibrated.

Thermal measurements were made by means of a Bunsen ice calorimeter essentially of the type described by Marshall and Keyes.[6] Several calibrations of the capillary, which agreed closely, were made using weighed threads of mercury. As a check upon the accuracy of the calorimeter it was calibrated under conditions of actual use by introducing known amounts of heat in the form of Bureau of Standards pure aluminum and zinc. An accuracy of 0.5% or better was indicated when the calorimeter was used under favorable conditions.

**Purification of Gases.**—The hydrogen used in this work was a compressed, electrolytic material which was purified by passage over heated copper turnings, solid potash, calcium chloride and phosphorus pentoxide in the order named. The helium initially about 96% pure, was further purified by drying over phosphorus pentoxide and very slow passage through activated charcoal[7] at liquid air temperature. The oxygen was prepared by the electrolysis of sodium hydroxide solution and then passed over heated copper oxide, a red hot platinum spiral, ascarite, calcium chloride and finally phosphorus pentoxide. Very pure oxygen was obtained in this way. Compressed ethylene was passed first over calcium chloride and then through a trap immersed in solid carbon dioxide and ether.

**Preparation of Catalysts.**—Chemically pure $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Th(NO_3)_4 \cdot xH_2O$, *e. g.*, 47.5% $ThO_2$, were used in the preparation of the catalysts. Prior to reduction the nitrates were ignited at a low temperature until completely changed to oxide. Continued stirring during the ignition resulted in very finely divided oxides. Thoria was incorporated by dissolving the nitrate in the melted nickel or copper nitrate. Supported catalysts were prepared by stirring carefully purified pumice (20–40 mesh) into a nitrate solution of suitable concentration, in such an amount that the liquid was completely absorbed. The mass was then subjected to low temperature ignition. Reduction was carried out by heating in hydrogen until less than 1 mg. of water could

[5] The word adsorption has been used throughout this paper to indicate what occurs when oxygen is brought into contact with a catalyst surface at 0°, and no idea of the way in which the oxygen is held is necessarily implied.

[6] Marshall and Keyes, THIS JOURNAL, **49**, 160 (1927).

[7] This charcoal was very kindly furnished us through the courtesy of Mr. L. M. Currie of the National Carbon Company, Cleveland.

be detected in a weighed phosphorus pentoxide tube in an hour. The temperature of reduction was regulated by means of a thermostat to within ±5°. Catalysts were reduced in bulbs about 18 mm. in diameter and 70 mm. long, and then sealed in place while still in an atmosphere of hydrogen. Once in place the catalysts were evacuated very completely at the temperature of reduction to remove adsorbed hydrogen.

**Heat of Adsorption Measurements.**—When it was certain that the calorimeter leak and the room temperature were constant, measurements were begun. Oxygen was admitted from the manometer, which was so calibrated that it measured both pressure and volume. This manometer was read by means of a cathetometer. A pressure of a few tenths of a mm. of helium was always present to ensure rapid attainment of thermal equilibrium. This was essential inasmuch as all but the last increment of oxygen was completely adsorbed. Therefore, dead space measurements were required only for the evaluation of final increments. Helium was used to determine the dead space values and was found not to be adsorbed, although nitrogen was adsorbed.

**Reaction Velocity Experiments.**—These measurements were made by a static method. The desired amount of a 1:1 ethylene–hydrogen mixture was admitted from the gas buret into the catalyst–manometer system and the reaction was followed by means of the pressure change. Manometer readings were taken every minute until the rate of pressure change became slow. This rate became very slow when reaction was 70 to 80% complete, and then the residual reaction mixture was quickly pumped off, as completely as possible at 0°, and collected. Final traces of the reaction mixture were removed by a slow heating usually to reduction temperature, at all times keeping the catalyst evacuated. Knowing the amount and composition of the reaction mixture initially introduced and the total amount finally pumped off, the extent of the reaction at the time of pumping was readily calculated from the volume change. Therefore, the pressure which would have existed in the system at the time of pumping, had no adsorption occurred, could be calculated. The difference between this calculated pressure and the actually observed pressure gave a measure of the total amount of gas adsorbed. By making the assumption that the magnitude of the total adsorption did not change appreciably between the time of 50% reaction and the time when the system was pumped, it was now possible to read off from a curve relating observed pressures and time, and with an allowance for the effect of adsorption, the time for half reaction. This half time has been used as a criterion of catalyst activity.

## Experimental Results

**A. Preliminary Work.**—Early measurements of the adsorption of oxygen on nickel indicated that this gas is very strongly adsorbed at 0° and that large thermal effects are involved. It was found impossible to desorb any oxygen by evacuation up to temperatures of 300 to 400°. A most interesting observation was made, however, when it was found that even though no oxygen could be pumped from the surface at these temperatures, yet the configuration of the adsorbed oxygen had undergone a marked change during the heating. This was indicated by the fact that the surface was now able again to adsorb large amounts of oxygen with only slightly reduced thermal effects. This behavior is all the more remarkable in view of the fact that the surface prior to heating was completely saturated at 0° with oxygen at atmospheric pressure.

The first measurements were made on pumice carrying 10% (0.5 g.) of

nickel which was reduced at 350°. For a promoter thoria, to the extent of 10% of the nickel present, was used. Only integral heats at pressures close to atmospheric were measured. On original surfaces values of the order of 98,000 and 95,000 cal. were obtained on the promoted and unpromoted catalysts, respectively. After three or four heatings of the oxygen saturated surfaces at 350°, both types of catalyst gave values of about 85,000 cal. On the original surfaces the promoted catalysts adsorbed nearly twice as much oxygen as the unpromoted, *e. g.*, 4.5 and 4.1 cc. against 2.4 cc. The first heating cut the adsorptive capacities of the promoted surfaces almost exactly in half while the unpromoted suffered slightly less. Heating a saturated promoted surface at 250° did not cause it to again adsorb oxygen at 0°.

Because of the relatively small amounts of oxygen adsorbed per unit volume when a support is present, it was next decided to investigate unsupported catalysts whose larger adsorptive capacities would make possible measurements upon partially saturated surfaces. Several unsupported promoted nickel catalysts were reduced at 300° and the heats of adsorption of increments of oxygen varying in size from 0.5 to 7 cc. measured. Catalyst 4 contained 6.4% thoria and weighed 7.086 g. It adsorbed 17.34 cc. of oxygen, before developing any pressure, with an average thermal effect of 92,000 cal. Heating to 300° for three hours caused the amount so adsorbed to decrease to 8.54 cc. with a concomitant thermal effect of 82,000 cal. Catalyst 5 contained a more nearly optimal amount of thoria, namely, 2%, and weighed 7.762 g. In nineteen successive increments it adsorbed 51.75 cc. of oxygen, before developing a pressure, with an average thermal effect of 101,000 cal. The individual heats of adsorption for the first half of the gas taken up were of similar magnitude giving an average value of 96,000 cal. The second half of the gas, however, was adsorbed with increasing thermal effects, a value as high as 108,000 cal. being obtained 7 cc. from the end. Heating this first surface to 300° for three hours caused the adsorption to drop to 11.83 cc. and the average heat of adsorption to 88,000 cal. With catalyst 7, which was similar to 5 but somewhat less active, the oxygen adsorption on the second surface was carried out at −38° and saturation reached at 16 cc. Upon warming up to 0° an additional 1 cc. was adsorbed with a thermal effect of 88,000 cal. It is interesting to note that oxygen is still adsorbed strongly at −38° and that the adsorptive capacity increases up to 0°.

In general, the values of the heats of adsorption obtained in this preliminary work probably correspond more nearly to integral than to differential values, and this is borne out by later experiments which will be presented in greater detail.

**B. Work on Nickel.**—In view of the results obtained in the preliminary work with nickel it was decided to investigate the phenomena some-

what more thoroughly. The apparatus was altered to conform with that already described and the accuracy[8] of the subsequent measurements is, therefore, somewhat greater.

Nickel catalysts 8 and 12 were prepared by reduction at 300°. The former was nickel alone while the latter contained 2% of thoria. The behavior of these two preparations toward oxygen should be clear from Tables I and II. It is apparent that, with the exception of the original surface of the promoted catalyst, the thermal values remained essentially constant until a given surface became saturated. Such a constant thermal effect would be explained if at 0° oxygen were adsorbed strongly over a considerable range of types of surface. If so the first increment of the oxygen would be almost entirely adsorbed by the uppermost layers of the catalyst with which it first came into contact, and successive increments would penetrate deeper down through the mass, giving average or nearly integral heats. Assuming that such values should be identical, a check is offered upon the relative accuracy of the measurements by an intercomparison of the observed values. Upon saturation of the lowest layers of the catalyst, the observed rapid rise in pressure and sharply diminished thermal effect would be anticipated. Prior to the appearance of a pressure, the adsorption was almost instantaneous. This pressure decreased slowly with time and the rate was not appreciably increased by augmenting the oxygen pressure. The equilibrium pressure of the adsorbed oxygen was far too low to measure in the manometer. That this pressure is substantially zero, however, was demonstrated by pumping the unadsorbed gas from the catalyst bulb and then allowing the closed system to stand as long as forty-eight hours, when not the slightest trace of gas could be detected in a large Toepler pump.

The promoter effect of thoria in No. 12 is apparent both in the larger adsorptive capacity and in the greater thermal values of this catalyst as compared with 8. Although the average heat of adsorption is less than a thousand calories higher on 12, yet that there is a real qualitative difference in surface is indicated by the considerable rise in the individual heats observed in the later increments on the promoted catalyst. The reason for this is not apparent although 5, which was also promoted, showed a similar phenomenon.[9] The effects produced by heating surfaces previously

[8] Under the most favorable conditions, as illustrated by the heats of adsorption with rapidly and completely adsorbed oxygen on nickel, a relative accuracy of the order of 1% seems probable. In the case of copper where the adsorption is complete but somewhat slower, a relative accuracy of about 2 to 3% is indicated. Final values on copper are least accurate. The absolute accuracy of the measurements while somewhat less should not be materially so.

[9] No evidence of incompletely desorbed hydrogen has been obtained in any of this work. The first few values of the heat of adsorption on an original surface have not been abnormal; furthermore, no water could be detected by pumping at temperatures up

saturated with oxygen at 0° at several temperatures for different times should be quite apparent from Tables I and II. After the first heating, in which the promoted catalyst suffered the more, there seems to be little evidence of any marked difference between the two catalysts in their response to subsequent heatings. Taken as a whole, however, the observations indicate that the extent of the transformation of oxygen adsorbed at 0° on an active nickel surface depends primarily upon the temperature of heating. The rate of transformation is negligibly slow at 250°, not quite complete in three hours at 300°, essentially complete in this time at 350°

TABLE I

OXYGEN ADSORPTIONS ON NICKEL

Catalyst 8. Weight, 9.037 g.

| | Pressure increase, mm. | Volume adsorbed, cc. N. T. P. | Heat evolved, cal. | Heat of adsorption, cal./mole |
|---|---|---|---|---|
| Original surface | | | | |
| 1 | 0.00 | 4.641 | 20.126 | 97,149 |
| 2 | .00 | 4.631 | 20.086 | 97,160 |
| 3 | 53.30 | 3.016 | 10.957 | 81,378 |
| | | 12.288 | 51.169 | |
| Second surface: produced by heating at 300° for three hours | | | | |
| 1 | 0.00 | 2.471 | 10.350 | 93,824 |
| 2 | .00 | 2.567 | 10.748 | 93,788 |
| 3 | 60.01 | 0.815 | 2.346 | 64,479 |
| | | 5.853 | 23.444 | |
| Third surface: produced by heating at 300° for three hours | | | | |
| 1 | 0.00 | 2.514 | 10.224 | 91,078 |
| 2 | 71.56 | 0.459 | 1.250 | 61,002 |
| | | 2.973 | 11.474 | |
| Fourth surface: produced by heating at 250° for three hours | | | | |
| 1 | 1.98 | 0.500 | .... | .... |
| Fifth surface: produced by heating at 350° for half an hour | | | | |
| 1 | 0.00 | 0.548 | 2.271 | 92,829 |
| 2 | .00 | 2.070 | 8.447 | 91,407 |
| 3 | 59.10 | 0.404 | 0.950 | 52,647 |
| | | 3.022 | 11.668 | |
| Sixth surface: produced by heating at 350° for three hours | | | | |
| 1 | 0.00 | 2.100 | 8.497 | 90,634 |
| 2 | 3.68 | 2.060 | 7.475 | 81,281 |
| | | 4.160 | 15.972 | |

to that of reduction and higher through a weighed phosphorus pentoxide tube after an oxygen adsorption.

TABLE II

OXYGEN ADSORPTIONS ON PROMOTED NICKEL

Catalyst 12. Promoter, 2% thoria. Weight, 6.982 g.

| | Pressure increase, mm. | Volume adsorbed, cc. N. T. P. | Heat evolved, cal. | Heat of adsorption, cal./mole |
|---|---|---|---|---|
| Original surface | | | | |
| 1 | 0.00 | 2.023 | 8.556 | 94,737 |
| 2 | .00 | 2.082 | 8.765 | 94,296 |
| 3 | .00 | 2.123 | 8.975 | 94,691 |
| 4 | .00 | 2.053 | 8.665 | 94,544 |
| 5 | .00 | 5.068 | 21.902 | 96,798 |
| 6 | .00 | 4.940 | 21.263 | 96,415 |
| 7 | .00 | 5.140 | 21.840 | 95,183 |
| 8 | .00 | 5.207 | 22.862 | 98,348 |
| 9 | .00 | 4.852 | 22.130 | 102,167 |
| 10 | .00 | 5.589 | 28.220 | 113,106 |
| 11 | 70.16 | 1.591 | 4.217 | 59,357 |
| | | 40.668 | 177.395 | |
| Second surface: produced by heating at 300° for three hours | | | | |
| 1 | 0.00 | 3.151 | 12.904 | 91,733 |
| 2 | .00 | 2.984 | 12.180 | 91,429 |
| 3 | .00 | 3.013 | 12.290 | 91,377 |
| 4 | .00 | 3.055 | 12.465 | 91,394 |
| 5 | 1.48 | 2.906 | 10.115 | 77,972 |
| | | 15.109 | 59.954 | |
| Third surface: produced by heating at 350° for three hours | | | | |
| 1 | 0.00 | 3.080 | 12.627 | 91,832 |
| 2 | .00 | 3.132 | 12.892 | 92,191 |
| 3 | .00 | 3.176 | 13.041 | 91,975 |
| 4 | .00 | 3.065 | 12.548 | 91,714 |
| 5 | .00[a] | 3.106 | 11.974 | 86,344 |
| | | 15.559 | 63.082 | |
| Fourth surface: produced by heating at 350° for three hours | | | | |
| 1 | 0.00 | 3.037 | 12.412 | 91,542 |
| 2 | .00 | 3.080 | 12.577 | 91,475 |
| 3 | .00 | 3.145 | 12.918 | 92,007 |
| 4 | .00 | 3.096 | 12.579 | 91,010 |
| 5 | 23.94 | 2.324 | 8.049 | 77,582 |
| | | 14.682 | 58.535 | |
| Fifth surface: produced by heating at 350° for eight hours | | | | |
| 1 | 0.00 | 3.149 | 12.866 | 91,533 |
| 2 | .00 | 3.172 | 12.920 | 91,239 |
| 3 | .00 | 3.121 | 12.760 | 91,580 |
| 4 | .00 | 3.183 | 12.913 | 90,859 |
| 5 | 35.12 | 1.972 | 6.272 | 71,254 |
| | | 14.597 | 57.731 | |

TABLE II (*Concluded*)

| | Pressure increase, mm. | Volume adsorbed, cc. N. T. P. | Heat evolved, cal. | Heat of adsorption, cal./mole |
|---|---|---|---|---|
| Sixth surface: produced by heating at 300° for three hours | | | | |
| 1 | 0.00 | 3.296 | 13.292 | 90,325 |
| 2 | .00 | 3.123 | 12.576 | 90,190 |
| 3 | 2.62 | 3.090 | 11.323 | 82,076 |
| | | 9.509 | 37.191 | |
| Seventh surface: produced by heating at 300° for twelve hours | | | | |
| 1 | 0.00 | 3.106 | 12.543 | 90,464 |
| 2 | .00 | 3.127 | 12.585 | 90,137 |
| 3 | 36.56 | 1.914 | 6.142 | 71,881 |
| | | 8.147 | 31.270 | |
| Eighth surface: produced by heating at 350° for three hours | | | | |
| 1 | 0.00 | 3.122 | 12.531 | 89,908 |
| 2 | .00 | 3.131 | 12.427 | 88,893 |
| 3 | 2.50 | 3.019 | 10.503 | 77,935 |
| | | 9.272 | 35.461 | |
| Ninth surface: produced by heating at 400° for three hours | | | | |
| 1 | 0.00 | 3.162 | 12.876 | 91,215 |
| 2 | .00 | 3.146 | 12.595 | 89,678 |
| 3 | .00 | 3.165 | 12.705 | 89,918 |
| 4 | .00[a] | 3.164 | 12.351 | 87,448 |
| | | 12.637 | 50.527 | |

[a] Pressure diminished slowly but reached zero within an hour.

and still faster at 400°. Raising the temperature of heating from 300 to 400° causes the transformation to become more comprehensive, as is evidenced by the increased adsorptive capacities and slight though definitely increased heats of adsorption. The magnitudes of these effects and especially the latter must be decreased by the known sintering effects produced when a catalyst is first brought to a temperature substantially above that of its production.

**C. Hydrogen Adsorption on Promoted Nickel Holding Previously Adsorbed Oxygen.**—Table III contains the results of four hydrogen adsorptions on No. 12 while it held varying amounts of oxygen previously adsorbed at 0°. The results of each oxygen adsorption are given, followed by that of the subsequent hydrogen adsorption. The final pressures for hydrogen were those observed twenty minutes after the gas was admitted. Only slow adsorption was taking place at the end of this time and the thermal values correspond to this interval of adsorption.

The first measurements were made upon the surface produced by heating to 400° for three hours, the ninth surface of No. 12. This surface

was probably not more than 25% saturated with oxygen and the heat of adsorption of 23,112 cal. indicates that hydrogen was largely adsorbed on nickel surface. No water could be removed by evacuation at 0°. When the catalyst was slowly heated up to 90° in hydrogen, a decrease in pressure was first noticed between 70 and 80°. Evacuated at 90°, 4.9 mg. of water was obtained, while the 3.211 cc. of adsorbed oxygen is equivalent to 5.1 mg. of water. The catalyst was then evacuated at 400° and the surface so produced about half saturated with oxygen at 0°. Although hydrogen admitted to this surface gave a somewhat higher thermal effect, yet it is probable that little water synthesis was involved. Heating in hydrogen as before indicated that reduction of adsorbed oxygen was occurring well below 60° and was complete at this temperature. Between 60 and 90° hydrogen produced no further effect. Evacuation at 90° gave 9.5 mg. of water whereas the 6.331 cc. of oxygen adsorbed is equivalent to 10.2 mg. of water. The catalyst was again evacuated at 400° and the surface so produced completely saturated at 0° with oxygen, unadsorbed oxygen removed, and hydrogen admitted. The much larger heat of hydrogen adsorption, 66,728 cal., and the definitely greater heat of oxygen adsorption on this surface strongly suggest that it was able to catalyze water formation at 0°. Upon standing overnight at 0°, all but 0.02 cc. of the gas disappeared and when this was removed the system showed no pressure in the manometer. No water could be desorbed by evacuation at 0°. Evacuation at 90, 150, 200 and 300° desorbed 0.5, 1.0, 1.7 and 2.8 mg. of water, respectively, or a total of 6 mg. The total amount of hydrogen which disappeared is equivalent to 5.5 mg. of water. The fourth surface was obtained by a final evacuation at 400° and it showed a quite similar behavior.

These experiments show definitely that oxygen adsorbed at 0° upon a nickel surface, which has been formed by heating relatively large amounts of oxygen previously adsorbed at 0°, *e. g.*, the treatments of No. 12 recorded in Table II, is still activated. That such surfaces should possess catalytic activity is not surprising when the magnitudes of their heats of the oxygen adsorption are considered. In the first two experiments the agreement between the amounts of water desorbed and the amounts of oxygen just previously adsorbed indicates that it is only this oxygen which is catalytically active. The large amounts of oxygen previously adsorbed but transformed by heating take no part in the reaction even at 90°. The increased heat of oxygen adsorption observed in the third experiment indicates that some reduction of nickel oxide by adsorbed hydrogen probably occurred during the evacuation between 90 and 400°. That the more active surfaces are able to catalyze the combination of hydrogen and adsorbed oxygen at 0° is suggested by the magnitudes of the hydrogen thermal effects, which are much too high for the heats of adsorption of this gas on nickel. The

greater difficulty in desorbing water from the last two surfaces also indicates their higher order of activity. Assuming water formation at 0° in the case of the two latter surfaces, heats of adsorption of water of the order of those obtained with platinum black catalysts[10] may be calculated.[11]

TABLE III

HYDROGEN ADSORPTION ON PREVIOUSLY ADSORBED OXYGEN

Catalyst 12. Weight, 6.982 g.

| | | | Pressure increase, mm. | Volume adsorbed, cc. N. T. P. | Heat evolved, cal. | Heat of adsorption cal./mole |
|---|---|---|---|---|---|---|
| I | Oxygen | 1 | 0.00 | 3.211 | 13.010 | 90,758 |
| | Hydrogen | 1 | 82.70 | 3.353 | 3.459 | 23,112 |
| Adsorbed oxygen removed by reduction, followed by evacuation up to 400° | | | | | | |
| II | Oxygen | 1 | 0.00 | 3.097 | 12.463 | 90,142 |
| | | 2 | .00 | 3.234 | 12.946 | 89,671 |
| | | | | 6.331 | 25.409 | |
| | Hydrogen | 1 | 44.50 | 3.180 | 3.987 | 28,085 |
| Adsorbed oxygen removed by reduction, followed by evacuation up to 400° | | | | | | |
| III | Oxygen | 1 | 0.00 | 5.582 | 23.217 | 93,167 |
| | | 2 | .00 | 5.660 | 23.446 | 92,796 |
| | | 3 | 98.13 | 2.366 | 8.196 | 77,580 |
| | | | | 13.608 | 54.859 | |
| | Hydrogen | 1 | 144.90 | 1.970 | 5.869 | 66,728 |
| Surface evacuated up to 400° | | | | | | |
| IV | Oxygen | 1 | 0.00 | 5.831 | 23.924 | 91,896 |
| | | 2 | .00 | 3.033 | 12.415 | 91,688 |
| | | 3 | 40.44 | 4.065 | 15.472 | 85,266 |
| | | | | 12.929 | 51.811 | |
| | Hydrogen | 1 | 41.60 | 1.721 | 5.239 | 68,194 |

**D. Work on Copper.**—On catalytically active copper oxygen was found to be both rapidly and strongly adsorbed at 0°, and the phenomena were in most respects quite similar to those on the nickel surfaces already studied. Only one marked difference was noted, namely, that the heats of oxygen adsorption on a given surface decreased as the amount of gas adsorbed increased. Therefore, the thermal measurements on copper probably represent more nearly differential heats than is the case with nickel.

[10] G. B. Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, **34**, 799 (1930).

[11] Using the value of 57,826 cal. ("International Critical Tables," Vol. V, p. 176) for the heat of formation of water and average values for the heats of oxygen adsorption of 92,981 and 91,792 cal. for the third and fourth surfaces, respectively, values for the heat of adsorption of water of 55,392 and 56,264 cal. are obtained. Such high values may in part explain the difficulty in removing adsorbed water.

The time required to reach thermal equilibrium in the calorimeter after admitting oxygen to a partially saturated surface varied from twenty-five to thirty minutes in the case of copper, whereas fifteen minutes sufficed in the case of nickel. Adsorbed oxygen could not be removed from copper surfaces at temperatures up to 400°. Heat treatments of a catalyst previously saturated with oxygen at 0° resulted in a surface capable of again

TABLE IV

OXYGEN ADSORPTIONS ON COPPER

| | Pressure increase, mm. | Volume adsorbed, cc. N. T. P. | Heat evolved, cal. | Heat of adsorption, cal./mole |
|---|---|---|---|---|
| Catalyst 9. Weight, 14.730 g. | | | | |
| Original surface | | | | |
| 1 | 0.00 | 2.446 | 8.317 | 76,164 |
| 2 | 82.94 | 2.006 | 5.510 | 61,527 |
| | | 4.452 | 13.827 | |
| Second surface: produced by heating at 170° for three hours | | | | |
| 1 | 0.00 | 0.485 | 1.344 | 62,100 |
| 2 | 1.16 | .453 | 1.250 | 61,832 |
| | | .938 | 2.594 | |
| Third surface: produced by heating at 250° for three hours | | | | |
| 1 | 0.00 | 0.454 | 1.403 | 69,216 |
| 2 | .00 | .470 | 1.486 | 70,822 |
| 3 | .00[a] | .477 | .... | .... |
| | | 1.401 | | |
| Catalyst 13. Wt. 12.219 g. | | | | |
| Original surface | | | | |
| 1 | 0.00 | 2.025 | 6.887 | 76,182 |
| 2 | 5.34 | 1.776 | 5.382 | 67,881 |
| | | 3.801 | 12.269 | |
| Second surface: produced by heating at 200° for three hours | | | | |
| 1 | 0.00[b] | 1.492 | 4.600 | 69,061 |
| Third surface: produced by heating at 250° for five hours | | | | |
| 1 | 0.00 | 1.520 | 4.712 | 69,440 |
| 2 | 18.90 | 0.958 | 2.966 | 69,351 |
| | | 2.478 | 7.678 | |
| Fourth surface: produced by heating at 300° for three hours | | | | |
| 1 | 0.00[b] | 1.548 | 4.863 | 70,368 |
| Fifth surface: produced by heating at 400° for three hours | | | | |
| 1 | 14.90 | 1.063 | 3.392 | 71,478 |

[a] This pressure was obtained only after standing overnight at zero degrees.
[b] Pressure diminished slowly but reached zero in about half an hour.

adsorbing oxygen strongly at this temperature. Undoubtedly this is a phenomenon similar to that observed with nickel. Experimental results are given in Tables IV and V. As would be anticipated from the behavior of nickel, the temperature to which an oxygen saturated copper catalyst is heated determines in large part the nature of the new surface formed. Temperatures between 170 and 400° were investigated. Excepting unpromoted copper at 300° and above, it appears that in this temperature range, the higher the temperature employed in heating, the greater the amount of oxygen subsequently adsorbed at 0°. Again excepting original surfaces, the heats of adsorption on the unpromoted catalysts show a marked tendency to increase as the temperature of heating is increased, while the promoted catalysts do not exhibit a definite trend; in fact the initial thermal values remain almost constant on all surfaces of No. 11 after the first.

The copper catalysts were reduced from the oxide at 175°. Catalysts 9 and 13 were of copper alone while 10 and 11 contained 7.5% thoria in each case. If the adsorptive capacities of these preparations are corrected, because of their considerable differences in weight, to the weight of 11, the effect of a promoter in increasing the extent of surface is seen to be very marked. Thus the original surfaces of 10 and 11 would adsorb 13.342

TABLE V

OXYGEN ADSORPTIONS ON PROMOTED COPPER

| | Pressure increase, mm. | Promoter, 7.5% thoria Volume adsorbed, cc. N. T. P. | Heat evolved, cal. | Heat of adsorption, cal./mole |
|---|---|---|---|---|
| Catalyst 10. Weight, 18.149 g. | | | | |
| Original surface | | | | |
| 1 | 0.00 | 4.551 | 16.844 | 82,904 |
| 2 | .00 | 4.536 | 15.214 | 75,130 |
| 3 | .00 | 4.478 | 13.099 | 65,524 |
| 4 | 75.80 | 2.356 | 6.118 | 58,167 |
| | | 15.921 | 51.275 | |
| Second surface: produced by heating at 175° for three hours | | | | |
| 1 | 0.00 | 2.498 | 7.833 | 70,240 |
| 2 | .00 | 2.488 | 7.366 | 66,323 |
| 3 | 13.18 | 2.133 | 5.275 | 55,396 |
| | | 7.119 | 20.474 | |
| Third surface: produced by heating at 300° for two hours | | | | |
| 1 | 0.00 | 2.524 | 7.676 | 68,122 |
| 2 | .00 | 2.503 | 7.615 | 68,148 |
| 3 | .00 | 2.514 | 7.343 | 65,426 |
| 4 | 22.46 | 1.861 | 4.745 | 57,113 |
| | | 9.402 | 27.379 | |

TABLE V (*Concluded*)

Promotor, 75% thoria

| | Pressure increase, mm. | Volume adsorbed, cc. N. T. P. | Heat evolved, cal. | Heat of adsorption, cal./mole |
|---|---|---|---|---|
| Catalyst 11. Weight, 15.209 g. | | | | |
| Original surface | | | | |
| 1 | 0.00 | 2.482 | 9.112 | 82,235 |
| 2 | .00 | 2.585 | 8.814 | 76,375 |
| 3 | .00 | 2.568 | 8.369 | 73,000 |
| 4 | .00 | 2.559 | 8.270 | 72,390 |
| 5 | .00[a] | 2.520 | 6.914 | 61,457 |
| | | 12.714 | 41.479 | |
| Second surface: produced by heating at 200° for three hours | | | | |
| 1 | 0.00 | 2.466 | 7.499 | 68,117 |
| 2 | .00 | 2.482 | 7.501 | 67,696 |
| 3 | .00[a] | 2.526 | 7.257 | 64,353 |
| | | 7.474 | 22.257 | |
| Third surface: produced by heating at 200° for three hours | | | | |
| 1 | 0.00 | 2.623 | 8.064 | 68,864 |
| 2 | .00 | 2.539 | 7.722 | 68,128 |
| 3 | .00[a] | 2.487 | 6.180 | 55,662 |
| | | 7.649 | 21.966 | |
| Fourth surface: produced by heating at 300° for three hours | | | | |
| 1 | 0.00 | 2.603 | 7.941 | 68,335 |
| 2 | .00 | 2.235 | 6.795 | 68,101 |
| 3 | .00 | 2.534 | 7.227 | 63,881 |
| 4 | .00[b] | 1.752 | 4.333 | 55,400 |
| | | 9.124 | 26.296 | |
| Fifth surface: produced by heating at 400° for three hours | | | | |
| 1 | 0.00 | 2.740 | 8.366 | 68,392 |
| 2 | .00 | 2.550 | 7.800 | 68,517 |
| 3 | .00 | 2.599 | 7.536 | 64,950 |
| 4 | 108.20 | 2.060 | 5.153 | 56,032 |
| | | 9.949 | 28.855 | |

[a] Pressure diminished slowly but reached zero in half an hour.

[b] Pressure reduced to zero by evacuating the catalyst.

and 12.714 cc. of oxygen, respectively, while 9 and 13 would adsorb but 4.597 and 4.731 cc., or approximately a third as much. The first heating has in each case caused a relatively larger decrease in the adsorptive capacity of the unpromoted catalyst, unlike nickel which, however, contained relatively smaller amounts of thoria. The great similarity of the second and third surfaces of 11 indicates that heating at 200° for the three hours is sufficient to maintain the *status quo*, while for promoted nickel a

temperature of 350° is required to do this. Considering the initial values for the heats of adsorption on the original surfaces of these catalysts, namely, 82,904 and 82,235 cal. against 76,164 and 76,182 cal., it is apparent that the promoted catalysts possess original surfaces of definitely higher quality than the unpromoted. After heating, the qualities of all of the surfaces became much more nearly alike.

**E. Reaction Velocities.**—In an endeavor to obtain information about any relations which might exist between the catalytic activity of a copper surface on the one hand and its capacity for adsorbing oxygen at 0° and the magnitudes of the incident thermal effects on the other, the following experiments were undertaken. As a convenient measure of catalytic activity the well-known ethylene–hydrogen reaction was chosen. Reaction velocity measurements, made by the manometric method, were followed, after thorough evacuation of the surface, by the customary determinations of the heats of oxygen adsorption. Preliminary velocity experiments on No. 10 showed that although a copper surface when saturated at 0° with oxygen possessed a negligibly small catalytic activity at this temperature, if the surface were heated activity returned. When velocity runs were attempted, however, on copper surfaces only partially saturated with oxygen at 0° this oxygen reacted. Ethylene–hydrogen reaction velocity measurements, with alternate oxygen adsorptions and heatings were made, however, on No. 11, a thoria promoted copper, and on No. 13, which was unpromoted. A comparison of reaction velocities with the extents and heats of oxygen adsorption is given in Table VI. The composition of the reaction mixture was always very nearly 1:1. Catalytic activity is taken as proportional to the reciprocal of the half time, and relative activities are calculated by arbitrarily giving the original surface of No. 11 the value of 100. The data in columns 4 and 5 of Table VI are not directly calculable from Tables IV and V because average heats of adsorption have been computed using an extrapolated value for the final thermal effect on a surface.

The experimental results show that whereas the original surface of No. 11 was decreased only about 41% in extent (as measured by the amount of oxygen adsorbed) as a result of heating the oxygen saturated surface at 200° for three hours, its catalytic activity was simultaneously decreased by 80%. The other half of the decrease is probably to be accounted for by the diminished heats of adsorption on the second surface. Relatively small changes in activity were produced by the second and fourth heatings, yet they are accompanied by significant changes in adsorptive capacity and / or heats of adsorption. The very much lower activity observed on the original surface of No. 13 shows thoria to be an effective promoter for copper. While this promoter effect is reflected in the relative extents of the original surfaces of these two catalysts, the average heat of adsorption

on No. 13 appears relatively too high. A comparison of the first thermal value on each original surface in this case seems the more significant. It is hardly to be expected that all of the oxygen adsorbed at 0° will define surface capable of participating in a given surface reaction. Only a certain fraction of the surface so defined will be involved in any particular reaction, and this fraction may well vary with the temperature, pressure and concentrations existing in the reaction system, also perhaps with the chemical composition of the catalyst surface. Pertinent thermal data should be calculated only from adsorption occurring on that fraction of the surface which is really active in catalysis. Thus while the data presented in Table VI indicate that relations exist between the behavior of a copper catalyst toward oxygen and the catalytic activity of the metal, these data are inadequate to define such relations quantitatively. It is considered, however, that they are sufficiently suggestive to justify further experiments with this end in view.

TABLE VI

A COMPARISON OF OXYGEN ADSORPTION CHARACTERISTICS WITH CATALYTIC ACTIVITY

| | Surface | Half time, $T$ (min.) | $1/T$ | Total oxygen adsorption, cc. N. T. P. | Average heat of adsorption, cal./mole | Relative activity |
|---|---|---|---|---|---|---|
| Catalyst 11 | Original | 3.5 | 0.284 | 12.118 | 75,323 | 100 |
| | Second | 17.4 | .058 | 7.195 | 67,776 | 20 |
| | Third | 16.0 | .063 | 6.216 | 68,371 | 22 |
| | Fifth | 15.5 | .065 | 7.530 | 68,256 | 23 |
| | Ninth | | | 2.486 | 55,510 | 0 |
| Catalyst 13 | Original | 76.8 | .013 | 3.438 | 74,874 | 5 |
| | Second | | | 1.492 | 69,061 | almost 0 |

## Discussion

The experimental work that has so far been carried out seems to substantiate the idea that oxygen is taken up by nickel and copper catalysts with characteristic effects. In the case of both of these surfaces oxygen is rapidly and irreversibly adsorbed at 0°. The relative amounts of oxygen so adsorbed are in line with the known relative activities of these catalysts. Initially nickel adsorbs over four times as much oxygen as an equal weight of copper. Adding thoria as a promoter increases the extent of the surface in the case of nickel more than four times, while the promoted copper shows nearly a three-fold increase. Thus in part the known superior activity of nickel over copper may be explained on the basis of greater surface; also, the function of a promoter in increasing the extent of surface is very clearly brought out.

The heats of oxygen adsorption on the surfaces studied also afford further insight into the relative activities of the catalysts. Thus the highest heats of oxygen adsorption occur on nickel surfaces while copper surfaces, as might be expected, show considerably lower thermal effects. The pres-

ence of thoria as a promoter causes a very definite increase in the heats of oxygen adsorption only on original catalyst surfaces. Regenerated unpromoted copper surfaces show somewhat higher thermal effects than similar regenerated promoted surfaces. In the case of nickel the initial thermal values on the original surface and all of the thermal values on the second surface of No. 8, the unpromoted catalyst, are higher than those on the corresponding promoted surfaces of No. 12. Such phenomena, together with the observed relative constancy of the heats of oxygen adsorption on a given nickel surface and the rapid decrease in these heats, with surface covered, on copper catalysts may be clues to the well-known specificity of catalysts. A maximum in heat of adsorption values has already been observed with very active nickel and hydrogen,[12] yet it is of interest that an irreversibly adsorbed gas like oxygen also shows it. In general, the magnitudes of the heats of oxygen adsorption are in the range of those found for platinum black catalysts.[13] On the basis of thermal effects alone the catalysts could be rated in the order of decreasing activity as nickel, platinum, copper, the order of their known activities for hydrogenations.

For all the catalysts studied, heating a surface which had been saturated with oxygen at 0°, in a suitable temperature range, caused a fresh unsaturation of surface to develop. It is well known that active nickel and copper surfaces are far from uniform and often highly non-uniform in character. Such surfaces are considered to possess areas of various degrees of unsaturation or catalytic activity (these two terms often, although not always, parallel each other). When oxygen comes into contact with an active surface at 0° it will first be adsorbed and then where the surface is sufficiently active may further react to form oxide at this temperature. On less active surface adsorbed oxygen may change to oxide only upon being heated in a suitable temperature range. Evidence that some oxide formation takes place on the original surfaces of the promoted catalysts at 0° is found in the magnitudes of the higher heats of oxygen adsorption there occurring. Thus values for the heat of formation, per mole of oxygen, of NiO range from 115,800 to 103,000 cal. and those for $Cu_2O$ from 87,600 to 79,826 cal. according to different observers.[14]

All surfaces after the first, *e. g.*, the regenerated surfaces, are much less extensive, as measured by oxygen adsorption, and are much less active as indicated both by heats of oxygen adsorption and reaction velocity measurements. The heats of adsorption on such surfaces are distinctly less than those required for oxide formation. Evidence that oxygen is *adsorbed*

[12] Fryling, *J. Phys. Chem.*, **30**, 818 (1926).

[13] G. B. Taylor, Kistiakowsky and Perry, *ibid.*, **34**, 799 (1930).

[14] Landolt-Börnstein-Roth-Scheel, "Tabellen," 5th ed., Vol. II, pp. 1530, 1531; "International Critical Tables," Vol. V, pp. 187, 192.

on these less active surfaces in activated form is found in the low temperatures required for its removal by reduction. Thus oxygen taken up by a nickel catalyst at 0° has been shown definitely to react with hydrogen below 90° and most probably as low as 0°, while large amounts of known oxide simultaneously present were unattacked. Similarly in the case of copper, oxygen adsorbed at 0° was removed at this temperature by hydrogen, while after heating the surface, such oxygen was inert. The minimum temperatures for the reduction of NiO and $Cu_2O$ are stated to be 220 and 155°, respectively.[15] Unless some activated form of oxide is present, therefore, the presence of *adsorbed* oxygen on the less active areas of the catalysts seems entirely probable. When a surface saturated with oxygen at 0°, is heated in a suitable temperature range, the following processes may occur (a) changes in the oxygen content of adsorption complex and oxides, (b) transformation of adsorption complexes to definite oxides, (c) physical changes such as sintering and the development of cracks or porosity in protective oxide films. Each of these processes conceivably may play a part in the regeneration of active surface during heating. Processes (a) and (b) if leading to combinations more rich in oxygen will cause previously covered surface to be exposed. The increased adsorptive capacities which the active surfaces studied have been found to exhibit toward oxygen at temperatures above 0° lend support to this idea. Evidence for process (b) has already been given, namely, that oxygen taken up at 0° is activated but becomes inactive after heating. Further evidence for this process is forthcoming if its mechanism is examined. The transformation of an adsorption complex to a fully formed oxide molecule must involve the rupture of metal–metal linkages and, therefore, create a fresh unsaturation of the metal surface. Such a surface will be in effect promoted by interspersed groups of oxide molecules. Furthermore, oxygen adsorbed on the more unsaturated metal surface should create a relatively less unsaturated surface upon heating than oxygen, initially adsorbed on more saturated surface, which upon heating to a sufficiently high temperature forms oxide only by the breaking of a greater number of metal–metal bonds. Therefore, it would be expected that within limits, the higher the temperature to which a given surface carrying adsorbed oxygen is heated, the greater the extent and the degree of unsaturation of the resultant surface. In spite of adverse sintering effects, it is experimentally found that with both nickel and copper increasing the temperature of heating has caused an increase in the extent of surface which is usually accompanied by a definite although sometimes small increase in the heats of adsorption. Furthermore, the large decrease in quantity and quality which a catalyst surface suffers as a result of the first oxygen adsorption and subsequent heat treatment is probably due to the relatively high degree

[15] Wright and Luff, *J. Chem. Soc.*, **33**, 540, 26 (1878).

of unsaturation of this surface and the consequent large amount of oxygen taken up as oxide at 0°. By process (c) fresh surface will be opened up if coherent oxide films are formed, but their extensive formation on highly non-uniform surfaces does not seem extremely probable. Process (b), which may be aided by (a), is therefore considered largely responsible for the regeneration of surface. Accordingly, it seems necessary to postulate that in the range of surface which takes up and holds oxygen strongly at 0°, there are combinations between the surface and oxygen varying from metal oxide on the most active areas to strongly *adsorbed* oxygen on the relatively less active portions.

While the alternate reaction velocity and heat of oxygen adsorption measurements are here confined to copper and a single reaction, it is not believed that the behavior found is limited to this particular combination. Further work is, therefore, being undertaken under different conditions, with other catalysts, and with other reactions in the hope of developing more completely the indicated relations and of obtaining a better insight into the mechanism of the regeneration of oxygen poisoned surfaces.

## Summary

1. The adsorption of oxygen at 0° on catalytically active nickel and copper surfaces has been studied. Relatively large amounts of this gas are rapidly and irreversibly taken up with a considerable evolution of heat. Molar heats of oxygen adsorption of the order of 98,000 cal. and higher, and 82,000 cal., have been obtained for promoted nickel and promoted copper, respectively.

2. A catalytically active surface, capable of again adsorbing relatively large amounts of oxygen at 0° with only moderately reduced thermal effects, is obtained simply by heating in a suitable temperature range a surface previously poisoned by saturation with oxygen at 0°. Evidence is advanced indicating that heating causes a change of *adsorbed* oxygen to stable oxide.

3. The amounts of oxygen taken up and the magnitudes of the heats of oxygen adsorption classify nickel and copper both promoted and unpromoted in their proper relative positions as catalysts. Additional light is thrown upon the function of a promoter of the irreducible oxide type.

4. Evaluation of the activity of copper catalysts on the one hand by reaction velocity measurements, and on the other by heats of oxygen adsorption and oxygen adsorbing capacity, indicates that definite relations exist between these properties.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF BRISTOL]

# THE ADSORPTION OF GASES AND VAPORS ON PLANE SURFACES

BY C. E. H. BAWN

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The adsorption of gases on solid surfaces has been the subject of numerous investigations. Most of the work, however, is concerned with the adsorption on non-uniform or amorphous surfaces, the accessible area of which is unknown. This has led to an uncertainty as to the thickness of the adsorbed layer, which is found to vary from a monomolecular layer[1] to a layer many molecules in thickness.[2] The decision on this point is complicated by the difficulty of obtaining a molecularly plane surface of large enough area upon which to measure the adsorption. The most suitable plane surface is that of a crystal. The present work, in which a large crystalline surface of mica has been employed, arose out of an investigation of the nature of the adsorbed film of vapors on mica surfaces.[3] These investigations were extended to confirm the important work of Langmuir[1] on the adsorption of gases on plane surfaces, and to throw further light on the nature of the monomolecular adsorbed film.

## Part I. The Adsorption of Carbon Monoxide, Argon and Oxygen on Mica at $P = 1 \times 10^{-4}$ cm. to $P = 2 \times 10^{-2}$ cm. at $T = 90°$ Abs. and $T = 193°$ Abs.

**Materials.**—The sheets of mica were obtained by splitting a specially selected piece of muscovite. The mica was cut into strips of definite size (11.3 × 1.8 cm.) by means of a very sharp razor, only pieces which showed no cracks and were uniform in thickness being selected. The strips were loosely held in the adsorption vessel in a thin silver wire frame, a similar frame being placed in the blank adsorption vessel. The total area of the mica was 6239 sq. cm.

**Oxygen** was obtained by heating pure potassium permanganate and was dried by passage through phosphoric oxide.

**Carbon monoxide** was prepared by dropping 100% formic acid onto concentrated sulfuric acid. It was passed through caustic potash to remove carbon dioxide and dried over phosphoric oxide.

**Hydrogen.**—This gas was carefully purified by the use of palladium and upon analysis was found to be 99.9% pure.

**Argon** was freed from other gases by passing through tubes containing (a) heated calcium oxide–magnesium, (b) heated copper oxide, the process being repeated until the gases showed that nitrogen and hydrogen were absent when the purity of the gas was tested in a discharge tube.

[1] Langmuir, THIS JOURNAL, 40, 1361 (1918); Zeise, *Z. physik. Chem.*, 136, 385 (1928).

[2] McHaffie and Lenher, *J. Chem. Soc.*, 1559 (1925); 1785 (1926); Lenher, *ibid.*, 272 (1927).

[3] To be published.

## Experimental

The adsorption was measured in the usual way by observing the decrease in the amount of gas, measured by change of pressure, which occurred when a known volume was admitted to the vessel containing the adsorbing surface.[1] The method possessed an advantage over that used by Langmuir in that the adsorption over a range of pressures could be measured in a single experiment by admitting successive amounts of gas. The pressures were measured by two McLeod gages, the capillary lengths of which had been calibrated and the volumes accurately determined. The first McLeod gage was used for pressures from $10^{-6}$ to $2 \times 10^{-2}$ cm. and the other from $10^{-2}$ to $2.5 \times 10^{-1}$ cm. The complete apparatus is shown in Fig. 1. The glass connections were constructed wholly of wide tubing 2 cm. in diameter, all joints being sealed glass and mercury U-seals used instead of stopcocks. The level of the mercury in the U-seals,

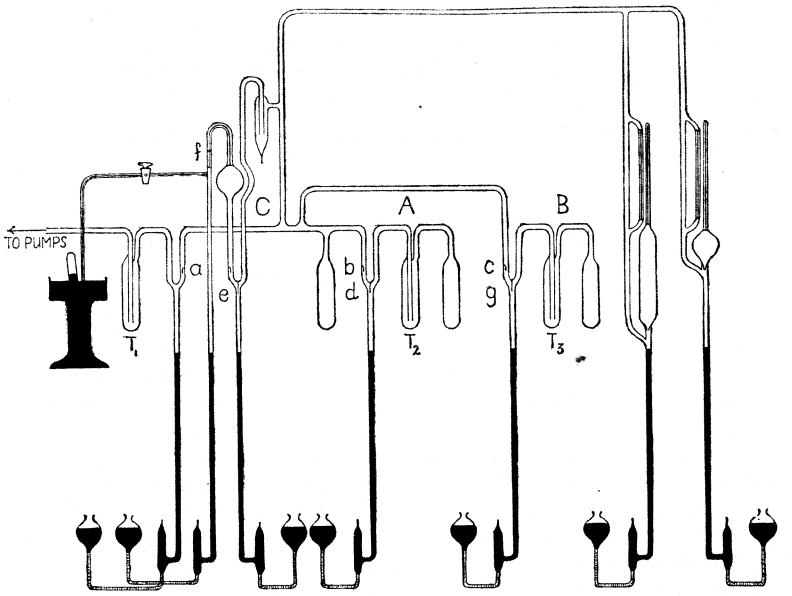


Fig. 1.

when either opened or closed, could be adjusted to the tips of pointers a, b, c, etc., sealed into the glass. The tap used to admit the gas was always cut off by a mercury seal during an experiment. $T_1$, $T_2$ and $T_3$ are traps which could be cooled in liquid air. The pumping system consisted of a glass mercury diffusion pump backed by a Hyvac oil pump. Two adsorption systems, A containing the mica, and B the blank were used. Each consisted of a mercury seal (bd or cg), liquid-air trap ($T_2$ or $T_3$) and adsorption vessel. The total volume and total glass surface were approximately the same in the two cases. The gas buret C was used both for calibration purposes and for admitting the gas during adsorption experiments.

**Calibrations.**—The volumes of the parts of the apparatus were determined by admitting a measured amount of hydrogen gas to the evacuated apparatus, measuring the pressure by the McLeod gage and applying Boyle's Law. Hydrogen gas was employed because no measurable adsorption of this gas on mica or glass occurred, as was shown by the fact that at all pressures of hydrogen the measured volumes agreed within

less than 1%. The volumes of the systems A and B were 962.3 and 965.1 cc., respectively.

As the adsorption experiments were conducted at 90°A. (liquid air) and 193°A. (solid carbon dioxide and alcohol), it was necessary to correct for the pressure change which occurs on cooling. Account has also to be taken of the "thermal molecular flow" discovered by Knudsen[4] which occurs at low pressures and in tubes of small diameter, when the mean free path is of the order of the diameter of the tube. The corrections were determined by the method of Langmuir, hydrogen gas being used. In Fig. 2, a typical calibration curve is given. The curve shows the variation with pressure of the ratio R, that of the pressure at room temperature to that of the pressure with the adsorption vessel containing the mica and trap (System A) cooled to liquid-air temperatures. The ratios for other gases were obtained from the hydrogen curve on the assumption that they would be the same at pressures at which the mean free paths were equal.

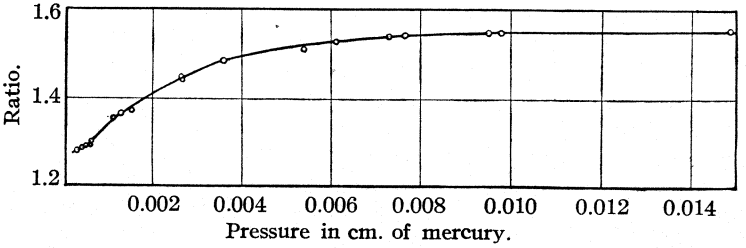


Fig. 2.—Calibration curve.

**Outgassing of the Surface.**—Langmuir[5] and Sherwood[6] concluded from an extensive series of investigations on the gases evolved from glass on heat treatment that the products below 300° were adsorbed gases, while at higher temperatures diffusion from the deeper layers and probably an actual decomposition of the glass occurred. The gases evolved from mica on heating are probably of a similar nature, the heating below 300° causing the removal of the adsorbed layers,[7] while above this temperature diffusion from the interior layers may occur, accompanied by a splitting of the crystal lattice. For these reasons, the temperature during the baking out process was maintained at 300°.

**Method of Experiment.**—This can best be understood by reference to Fig. 1. The mica was baked out for three hours, the system B being cut off by the U-seal cg. The trap $T_1$ was cooled in liquid air during this period and, for reasons discussed later, the trap $T_2$ was also cooled during the latter part of the baking out. The final pressure in the apparatus after baking out was always less than $10^{-6}$ cm. With the system A cut off by the U-seal bd, a quantity of gas was measured approximately in the gas buret C in order to obtain the necessary working pressure. The seal e was opened, the mercury surfaces leveled to a, f, e and b, and the pressure in this part of the system (say volume $v_1$) measured. The gas was now expanded to A (volume $v_2$), the mercury leveled to the pointer d and the equilibrium pressure measured. From this pressure, after application of the low temperature-pressure correction, the amount of gas in $V_1$ and $V_2$ together was found; the difference between this amount and the amount previously measured in $V_1$

[4] Knudsen, *Ann. Physik*, **31**, 305 (1910); **33**, 1435 (1910).

[5] Langmuir, THIS JOURNAL, **38**, 2283 (1916).

[6] Sherwood, *ibid.*, **40**, 1645 (1918).

[7] Langmuir found that the gases given off by mica at 300° corresponded to a double layer of water molecules and a single layer of carbon dioxide.

gives the amount of gas adsorbed by the mica and glass in A. The U-seal bd was now closed, and the mercury leveled to b. From a knowledge of the residual pressure in $V_1$ and $V_2$, and the volumes of the parts of the U-seal bd, and assuming that the gas in bd is divided proportionally between $V_1$ and $V_2$ on closing the seal, the total amount of gas left in $V_2$ was known. A second amount of gas was admitted to $V_1$ and the pressure measured. This was expanded to $V_2$ as before, the measurement of the total pressure giving the amount of gas now in $V_1$ and $V_2$. The difference between this amount and the amount of gas in $V_1$ and $V_2$ previously, gives the amount adsorbed due to the first increase in gas pressure. The addition of this amount to the former amount of adsorption is the total amount adsorbed at the second pressure. This process was repeated. With increase in pressure, the accuracy of the measurement of the small decrease in volume of gas became less and the series was usually discontinued at a pressure of $2 \times 10^{-2}$ cm. Values for higher pressures were obtained by admitting the gas at the required pressure and measuring the total adsorption. It was found that the amount of the adsorption at any pressure was independent of the number of increments by which the pressure was built up or whether the adsorption was measured directly at that pressure.

The procedure for the determination of the amount of gas adsorbed by the glass blank was exactly the same as described above, the adsorption vessel containing the mica being cut off during these experiments.

**Rate of Adsorption.**—In view of a recent publication by H. S. Taylor[8] the time required for adsorption equilibrium to be reached is of interest. At 193°A. equilibrium was reached very rapidly, in fact, no change of pressure was observed three minutes after admitting the gases. Owing to the time taken in reading the pressure by means of the McLeod gage, it was impossible to investigate the pressure change during this period. Table I shows two series of results for carbon monoxide at 193°A. At 90°A., however, the time taken to reach equilibrium was much longer. A typical series of results for carbon monoxide is as given in Table II and shown graphically in Fig. 3. It is observed that equilibrium is reached after forty-five minutes. These results are in agreement with the work of Taylor, who postulates the existence of an activation energy for adsorption

TABLE I

RESULTS FOR CARBON MONOXIDE AT 193°A.

| Time after admitting gas, min. | Pressure, cm. | Amt. adsorbed, cc. |
|---|---|---|
| 3 | 0.00293 | 0.00136 |
| 35 | .00291 | |
| 55 | .00292 | |
| 3 | .000654 | .... |
| 13 | .000648 | |

TABLE II

RESULTS FOR CARBON MONOXIDE AT 90°A.

| Time after admitting gas, min. | Pressure, cm. | Amt. adsorbed, cc. |
|---|---|---|
| 2 | 0.00532 | 0.0132 |
| 7 | .00439 | .0317 |
| 13 | .00302 | .0595 |
| 18 | .00218 | .0763 |
| 23 | .00163 | .0874 |
| 32 | .00110 | .0984 |
| 47 | .000801 | .1039 |
| 53 | .000653 | .1057 |
| 67 | .000606 | .1075 |
| 78 | .000566 | .1082 |

[8] Taylor, THIS JOURNAL, **53**, 578 (1931).

processes, and therefore a slow rate of adsorption. The observed rate of adsorption could not be attributed to "slow diffusion of the gas through spaces between the mica strips," as Langmuir[9] had assumed, otherwise the effect would have been noticed at 193°A. The data were insufficient to allow a calculation of the energy of activation to be made.

In all the experiments described below, the pressure was recorded fifteen minutes after admitting the gas to the mica at 193°A. and after sixty-five minutes at 90°A.

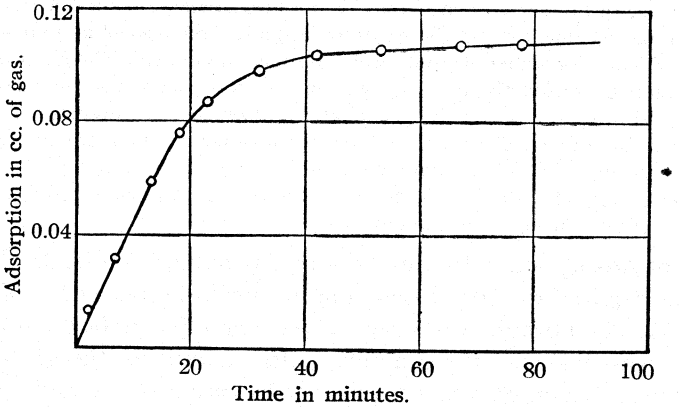


Fig. 3.—Curve showing the rate of adsorption of carbon monoxide at 90°A.

**Summary of Experimental Results.**—The results for the adsorption of three gases on mica at temperatures 90°A. and 193°A. are given in Tables III–VIII. In the first two columns, the pressure and the amount of gas adsorbed on the mica and glass together are given; columns III

TABLE III

CARBON MONOXIDE AT 193°A.

| Expt. | Adsorption on mica and glass | | Adsorption on glass blank | | Corrected results for adsorption on mica | |
|---|---|---|---|---|---|---|
| | Press., cm. | Adsorption, cc. | Press., cm. | Adsorption, cc. | Press., cm. | Adsorption, cc. |
| 17 | 0.00121 | 0.00075 | 0.00252 | 0.00080 | 0.002 | 0.00200 |
| | .00326 | .00315 | .00534 | .00283 | .004 | .00400 |
| | .00597 | .00624 | .00829 | .00434 | .006 | .00630 |
| | .00932 | .0104 | .0120 | .00553 | .008 | .00825 |
| | .0138 | .0150 | | | .010 | .01038 |
| | .0225 | .0229 | | | .012 | .01250 |
| 18 | .00274 | .00278 | .00387 | .00113 | .014 | .01438 |
| | .00871 | .00981 | .00587 | .00242 | .016 | .01653 |
| | .0139 | .0146 | .00983 | .00309 | .018 | .01838 |
| | .0205 | .0213 | .0145 | .00351 | .020 | .02013 |
| | | | | | .022 | .02163 |

[9] Ref. 1, p. 1381.

TABLE IV

CARBON MONOXIDE AT 90°A.

| Expt. | Adsorption on mica and glass: Press., cm. | Adsorption on mica and glass: Adsorption, cc. | Adsorption on glass blank: Press., cm. | Adsorption on glass blank: Adsorption, cc. | Corrected results for adsorption on mica: Press., cm. | Corrected results for adsorption on mica: Adsorption, cc. |
|---|---|---|---|---|---|---|
| 22 | 0.000566 | 0.1082 | 0.00132 | 0.00498 | 0.00025 | 0.070 |
| | .00105 | .1339 | .00205 | .00698 | .0005 | .101 |
| | .00453 | .1717 | .00344 | .00797 | .001 | .130 |
| | .00545 | .1769 | .00465 | .00820 | .0015 | .141 |
| | .00791 | .1889 | .00852 | .01114 | .002 | .147 |
| | .01059 | .1960 | | | .003 | .156 |
| 23 | .000123 | .0544 | | | .004 | .160 |
| | .000197 | .0893 | | | 005 | 165 |
| | .00756 | .1230 | | | 006 | 169 |
| | .00228 | .1490 | | | .007 | .173 |
| | .00713 | .1785 | | | .008 | .177 |
| | | | | | .009 | .181 |
| | | | | | .010 | .182 |

and IV contain the corresponding results for the blank adsorption vessel and columns V and VI the pressure–adsorption values for the mica surface only. The latter results were obtained from the plots of the figures in columns I and II, and III and IV, and subtraction of the two curves. These results were read off from the final curve. This was simplified by the fact that the adsorption on the blank was so small that the isotherm was usually linear. The adsorption isotherms are shown in Figs. 4, 5 and 6. In the case of the adsorption of argon the three curves, total adsorption on mica and glass, blank adsorption and the final corrected curve, are given as an illustration of the method. Curve II, Fig. 4, also shows the plots of two series of results for the adsorption of carbon monoxide by the blank adsorption vessel.

The two series of results obtained in Experiments 17 and 18 and Experiments 22 and 23 for the adsorption of carbon monoxide at 193 and 90°A., respectively, agreed so well that the corrected results given in columns V and VI are the mean of the two series in each case. The same procedure applies to Experiments 33 and 34, Table VIII, for the absorption of argon at 90°A.

TABLE V

OXYGEN AT 193°A.

| Expt. | Adsorption on mica and glass: Press., cm. | Adsorption on mica and glass: Adsorption, cc. |
|---|---|---|
| 43 | 0.002318 | 0.00200 |
| | .00479 | .00490 |
| | .00625 | .00641 |
| | .00989 | .01025 |
| | .01391 | .01328 |
| | .01665 | .01483 |

TABLE VI

OXYGEN AT 90°A.

| Expt. | Adsorption on mica and glass: Press., cm. | Adsorption on mica and glass: Adsorption, cc. |
|---|---|---|
| 41 | 0.00232 | 0.00619 |
| | .00356 | .00952 |
| | .00560 | .0126 |
| | .00755 | .0156 |
| | .01186 | .0204 |
| | .01295 | .0208 |

The adsorption of oxygen at 193°A. on the glass blank was so small that it was impossible to measure the small decrease in volume of gas which occurred on admitting successive quantities of gas. The amount adsorbed on the glass was not greater than $8 \times 10^{-4}$ cc. or less than 5% of the adsorption on the mica surface. No correction was made for this either at 193°A. or 90°A.

TABLE VII

ARGON AT 193°A.

| Expt. | Adsorption on mica and glass | | Adsorption on glass blank | | Corrected results for adsorption on mica | |
|---|---|---|---|---|---|---|
| | Press., cm. | Adsorption, cc. | Press., cm. | Adsorption, cc. | Press., cm. | Adsorption, cc. |
| 37 | 0.00180 | 0.00162 | 0.00409 | 0.0006 | 0.001 | 0.0010 |
| | .00344 | .00358 | .00601 | .00110 | .0025 | .0019 |
| | .00561 | .00585 | .00844 | .00125 | .0035 | .0028 |
| | .00833 | .00841 | .01480 | .00165 | .005 | .00425 |
| | .01140 | .01165 | | | .007 | .00590 |
| | .01460 | .0150 | | | .0095 | .00825 |
| | | | | | .0115 | .0100 |
| | | | | | .013 | .01125 |
| | | | | | .0145 | .01270 |

TABLE VIII

ARGON AT 90°A.

| Expt. | Adsorption on mica and glass | | Adsorption on glass blank | | Corrected results for adsorption on mica | |
|---|---|---|---|---|---|---|
| | Press., cm. | Adsorption, cc. | Press., cm. | Adsorption, cc. | Press., cm. | Adsorption, cc. |
| 33 | 0.00103 | 0.00257 | 0.00088 | 0.00158 | 0.001 | 0.00252 |
| | .00162 | .00630 | .00386 | .00296 | .003 | .00550 |
| | .00319 | .0115 | .00489 | .00374 | .005 | .01375 |
| | .00500 | .0173 | .00734 | .00606 | .007 | .01875 |
| | .00815 | .0280 | .00988 | .00751 | .009 | .0230 |
| | .0113 | .0344 | | | .010 | .0245 |
| 34 | .00164 | .00559 | | | .011 | .02575 |
| | .00340 | .0112 | | | .0115 | .0265 |
| | .00507 | .0170 | | | | |

In the preliminary experiments with carbon monoxide, in which the traps $T_1$ and $T_2$ were not cooled, the adsorption was very slight and varied greatly with the time of beginning the run after the baking process. At this time, the surface was baked out overnight and allowed to cool during the night. The slight adsorption was thought to be due to the long period of cooling, mercury vapor having diffused into the adsorption vessel and in some way "blocking" the surface. It has been suggested since that this effect may have resulted from the occurrence of a different kind of adsorption with a high activation energy, such as that observed by Garner and Kingman[10] and fully discussed by Taylor.[8] This takes place at the higher temperature during the process of baking out. The difficulty was over-

[10] Garner and Kingman, *Nature*, **126**, 352 (1930); Kingman, *ibid.*, **127**, 742 (1931).

come by cooling the trap $T_1$ in liquid air during the baking out and also $T_2$ during the latter part of the baking out process. $T_2$ was maintained in

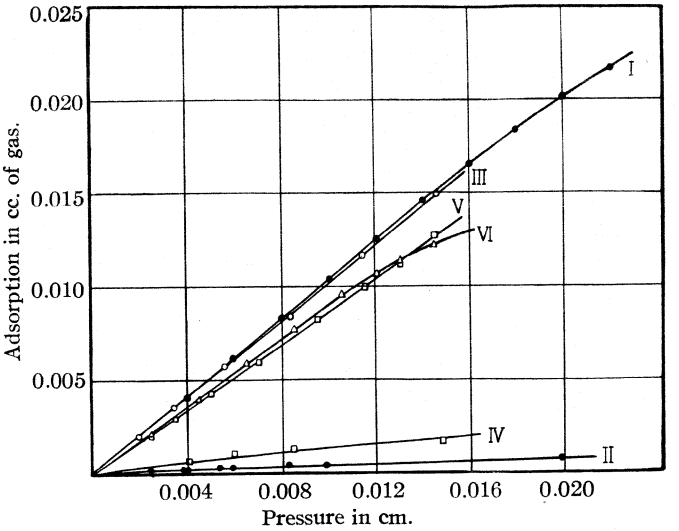


Fig. 4.—Adsorption of gases at 193°A.: Curve I, carbon monoxide on mica; curve II, carbon monoxide on glass blank; curve III, argon on glass and mica; curve IV, argon on glass blank; curve V, argon on mica; curve VI, oxygen on mica.

liquid air to constant level throughout the investigations, both for results at 90°A. and at 193°A. In the experiments described, the mica was baked out on the same day as the experiment was made, being allowed

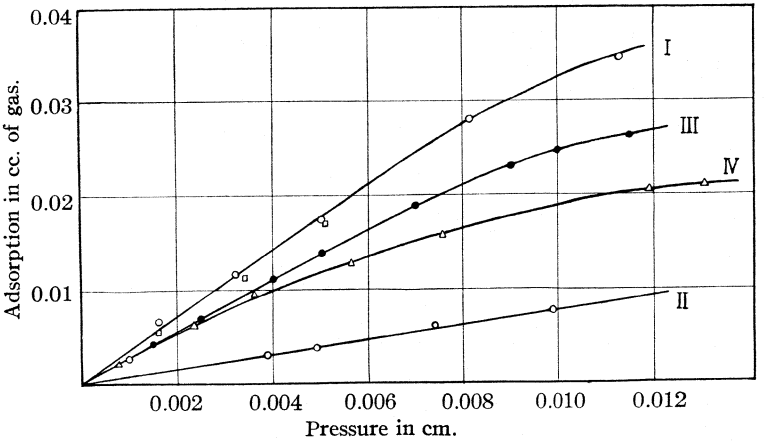


Fig. 5.—Adsorption of gases at 90°A.: Curve I, argon on glass and mica; curve II, argon on glass blank; curve III, argon on mica; curve IV, oxygen on mica.

to cool for two hours before the commencement of the experiment. With this standard procedure, the isotherms were quite reproducible, especially after the cooled surface had been treated with the gas to be adsorbed several times and baked out each time. It was generally found that lower values of the adsorption were obtained in the earlier experiments although the same form of isotherm was always obtained.

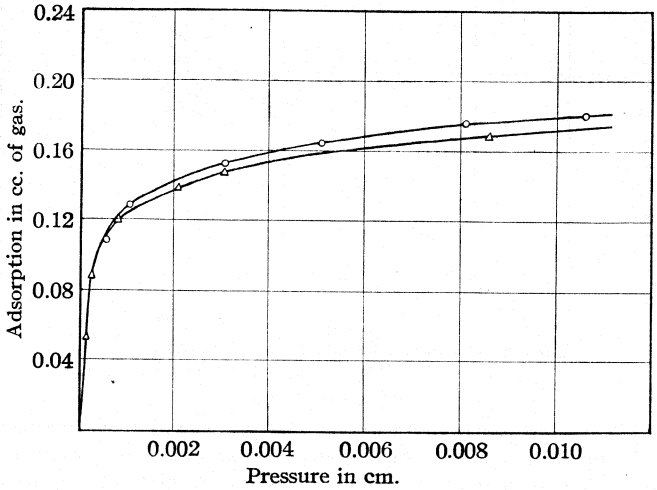


Fig. 6.—Adsorption of carbon monoxide on mica at 90°A. (two series).

**Adsorption at Room Temperature.**—An attempt was made to measure the adsorption of carbon monoxide at room temperature. The amount adsorbed, however, was so very little that up to a pressure of 0.016 cm. the loss of gas was of the order of ± 0.00005 cc. to 0.0001 cc. The area of surface covered was therefore never more than 0.5% at room temperature. These values also indicate the order of accuracy of the measurements, as at low pressures the amount of gas could always be checked up to ± 0.0001 cc.

## Discussion

The adsorption equation deduced by Langmuir[1] and Hückel[11] may be expressed in the form

$$x = \frac{c_1 c_2 p}{1 + c_2 p} \qquad (1)$$

$c_1$ and $c_2$ are constants at any given temperature; $c_1$ is adsorption maximum for the surface, $c_2$ is average time of stay of molecule on the surface.

Two important facts follow from this equation. (1) At low pressures, $c_2 p$ is negligible compared to unity and the equation reduces to

$$x = c_1 c_2 p \qquad (2)$$

[11] Hückel, "Adsorption and Kapillar-Kondensation," Leipzig, 1928.

that is, the adsorption is directly proportional to the pressure. (2) At high pressures, $c_2p$ is large compared to unity so that the amount adsorbed reaches a limiting value $c_1$.

**Adsorption at 90°A.**—The results for the adsorption of carbon monoxide at liquid-air temperature (Fig. 5) show clearly the existence of the saturation value for the surface. The Langmuir equation is obeyed very closely. The data for oxygen (Fig. 5, curve IV) are also in agreement with the Langmuir equation, although this gas is adsorbed to a far less extent than carbon monoxide. In the case of argon (Fig. 5, curve II), however, the equation is not followed over the whole pressure range studied. The isotherm is nearly linear up to pressures $5 \times 10^{-3}$ cm., but the Langmuir equation holds above a pressure of $8 \times 10^{-3}$ cm. Langmuir[12] found that in the case of the adsorption of carbon monoxide on glass the simple equation (1) had to be modified in order to take into account the existence of two distinct stages of adsorption. In a similar manner the adsorption of argon on mica can be explained if we assume that the adsorption occurs on more than one kind of "elementary space." The adsorption equation may then be written

$$x = k_1 \frac{c_1 c_2 p}{1 + c_2 p} + k_2 \frac{c_1' c_2' p}{1 + c_2' p} + \text{etc.} \qquad (3)$$

where $k_1$ and $k_2$, etc., represent the fraction of the various surfaces. The actual form of the resulting isotherm depends on the magnitude of the terms in this equation. No other simple equation has been found to cover the adsorption of argon from pressures $1 \times 10^{-4}$ cm. to pressure $1.2 \times 10^{-2}$ cm.[13]

Writing equation (1) in the form

$$\frac{p}{x} = \frac{1}{c_1 c_2} + \frac{p}{c_1} \qquad (4)$$

it will be seen that the plot of $p/x$ against $p$ should be a straight line, the slope of which is $1/c_1$. The values of $c_1$, the saturation for the surface in molecules adsorbed per sq. cm., are given in Table IX.

TABLE IX

| Gas | $c_1$ (moles/sq. cm.) | $\beta$ % surface covered at saturation | Heat of adsorption, cal. |
|---|---|---|---|
| $O_2$ | $0.180 \times 10^{15}$ | 23 | 186 |
| A | $.233 \times 10^{15}$ | 30 | 334 |
| CO | $.745 \times 10^{15}$ | 113 | 1048 |

The values of $\beta$, percentage surface covered at saturation, are also given, the number of molecules required to form a monomolecular layer being estimated from the diameter of the molecules in the liquid state. The

[12] Langmuir, Ref. 1, p. 1388.

[13] Langmuir gives the results for the adsorption of argon at two pressures only; hence, no comparison with the complete form of the isotherm can be made.

surface is completely covered in the case of carbon monoxide,[14] but with argon and oxygen only about one-fourth of the surface is covered. Comparison with the adsorption values obtained by Langmuir for these gases shows that the order of the amounts necessary to saturate the surface, namely, carbon monoxide, argon, oxygen—carbon monoxide being the most and oxygen the least adsorbed—is the same in both cases. The saturation value of the adsorption is, however, two to three times greater than for the mica used by Langmuir.

In order to account for the variation in $\beta$ for different gases, Langmuir assumed that the surface was not homogeneous, but was composed of different kinds of elementary spaces, each possessing a different adsorptive power. The surface of muscovite consists of a complex distribution of K, Al, Si, and O and H atoms, the layers of mica according to Pauling[15] being held together by potassium atoms. Several kinds of adsorption would therefore be expected. The low saturation value for oxygen may result from the oxygen being adsorbed only on the metallic atoms in the surface while carbon monoxide, being unsaturated, is adsorbed on all types of surface atoms, giving a complete layer. In the case of argon, the adsorption on more than one kind of elementary space has already been discussed.

**Adsorption at 193°A.**—It is evident from Fig. 4 that for small amounts adsorbed corresponding to less than one-tenth of the measured area of the surface covered, the amount adsorbed is directly proportional to the pressure. For small amounts adsorbed, Hückel[16] deduces the equation

$$\frac{Na}{Ng} = \Delta e^{\varphi/RT} \qquad (5)$$

$Na$ being number of g. moles adsorbed per sq. cm., $Ng$ being number of g. moles per cc. in gas phase, $\Delta$, thickness of adsorbed layer and $\varphi$, heat of adsorption.

The amount adsorbed is therefore directly proportional to the pressure if the surface is homogeneous, and thus $\varphi$ is constant, and if the area does not alter during adsorption. The variation of the heat of adsorption for different amounts adsorbed has been demonstrated by Garner and his coworkers,[17] Taylor,[18] *et al.*, but in such cases the measurements were made on active surfaces, for which the heat of adsorption is high. In this case it may be assumed that $\varphi$ remains constant for small amounts adsorbed, as is indicated both by the linear variation of the amounts adsorbed with pressure and the low value obtained for the heat of adsorption.

[14] This value is calculated from the measured surface, which is probably an underestimation of the true surface area.

[15] Pauling, *Proc. Nat. Acad. Sci.*, **16**, 123 (1930).

[16] Ref. 11, p. 58.

[17] Garner, Bull and Hall, *J. Chem. Soc.*, 837 (1931).

[18] Taylor and Kistiakowsky, *Z. physik. Chem.*, **A125**, 341 (1927).

From the logarithmic form of equation (5)

$$\log \frac{Na}{Ng} = \log \Delta + \frac{\varphi}{RT}$$

the plot of log $Na/Ng$ against $1/T$ gives a straight line, the slope of which is $\varphi/R$. The values of $\varphi$ determined in this manner from the results at two temperatures are given in Table IX.

Above pressures $8 \times 10^{-3}$ cm., the isotherms for oxygen and carbon monoxide show a marked curvature and in this region the data are in agreement with Langmuir's equation. Extrapolation as before to the saturation value gives the approximate values for the percentage surface covered at saturation as CO 82%, $O_2$ 16%. The isotherm for argon (Fig. 5, curve III), is linear up to the highest pressure measured.

The saturation value on Langmuir's theory is attained with the formation of a monomolecular layer and should therefore be independent of temperature except in so far as the number of elementary spaces per unit area ($N_0$) does not vary with temperature. The results at 90 and 193°A. for carbon monoxide and oxygen confirm the observations of Langmuir at 90 and 155°A. in that the saturation value is largely dependent on temperature. The temperature variation of the values of the constants $c_1$ and $c_2$ in the Langmuir equation have recently been examined theoretically by Zeise,[19] Polanyi[20] and Wilkins and Ward.[21] The latter authors, following the work of Volmer[22] and his collaborators, assume that the adsorbed molecules possess lateral motion over the surface and show that the temperature coefficient of the saturation maximum is that of the coefficient of expansion of a gas at constant pressure. This motion of the adsorbed molecules may occur when the oscillatory motion of the molecules tangential to the surface is large enough to allow the molecules to jump from one elementary space to another. The present author has obtained some direct evidence that this occurs in the case of acetone vapor adsorbed on mica at room temperatures.[23]

## Part II. The Adsorption of Acetone Vapor on Mica at Pressures $2 \times 10^{-6}$ cm. to $1\text{–}2 \times 10^{-2}$ cm. and at 292°A.

The apparatus described in Part I, with slight modifications, was employed. Although the McLeod gage is not the most suitable for use with vapor, the gage can be used to measure the pressures of vapors accurately if the mercury levels in the two capillaries of the McLeod gage are nearly level when taking a pressure reading. The pressures measured on two

[19] Zeise, *Z. Elektrochem.*, **35**, 426 (1929).
[20] Polanyi, *Z. physik. Chem.*, **A138**, 439 (1929).
[21] Wilkins and Ward, *ibid.*, **A144**, 259 (1929).
[22] Volmer and Adhikari, *ibid.*, **119**, 46 (1926).
[23] To be published.

McLeod gages of different volumes agreed closely. The system for admitting the acetone consisted of a U-tube with small bulb in series. The acetone was contained in the evacuated bulb in a small sealed tube which was easily broken by gentle heating. The vapor liberated was frozen out in the U-tube by means of liquid air and the system again evacuated to remove any air which may have been dissolved in the acetone. The experimental procedure for measuring the adsorption was as described previously, the adsorption vessel being maintained at constant temperature by immersion in a Dewar vessel containing water.

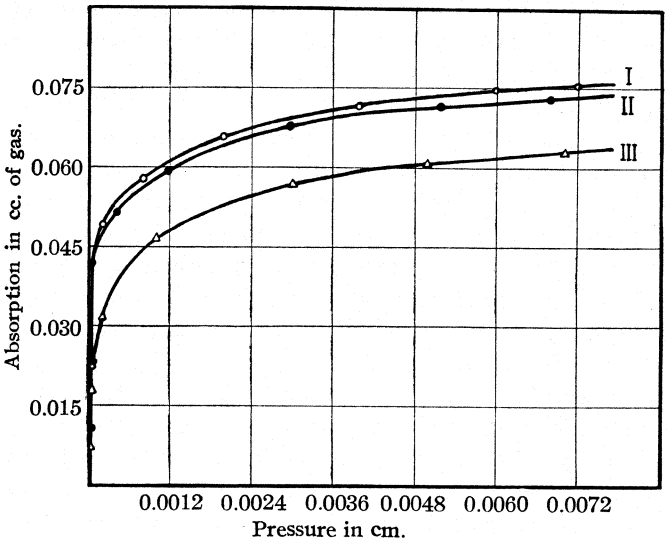


Fig. 7.—Adsorption of acetone on mica at 290°A.

In order to obtain concordant results for a series of adsorptions, it was necessary to keep the trap $T_1$ cooled by liquid air during the whole period of baking out. Without this trap, the pressure in the apparatus after baking out was still $10^{-4}$ cm., but as soon as $T_1$ was cooled, the pressure fell within ten minutes to $4 \times 10^{-6}$ cm. The isotherms obtained are given in Fig. 7. Curve III shows the decrease in the amount of adsorption resulting through cooling the trap $T_1$ during the last half hour of the baking-out only. With no trap, the saturation value was reached when 0.035 cc. of acetone had been adsorbed. Increased periods of baking out produced no further increase in the final saturation value than that reached in Experiments 27 and 28, Table X, and plotted in Fig. 7, curves I and II.

No measurements of the rate of adsorption were made other than to ascertain the time taken to attain equilibrium. This was reached in less than fifteen minutes after the vapor had been admitted to the adsorption vessel.

TABLE X

ACETONE ON MICA AT 292°A.

| Expt. | Adsorption on mica, Press., cm. | Adsorption, cc. | Adsorption on glass, blank Press., cm. | Adsorption, cc. | Corrected results for adsorption on mica Press., cm. | Adsorption, cc. |
|---|---|---|---|---|---|---|
| 27 | $2.3 \times 10^{-6}$ | 0.0109 | 0.00051 | 0.00181 | $2.3 \times 10^{-6}$ | 0.0109 |
| | $1.4 \times 10^{-5}$ | .0231 | .00110 | .00204 | $1.4 \times 10^{-5}$ | .0231 |
| | 0.000135 | .0418 | .00202 | .00267 | 0.000135 | .0418 |
| | .000634 | .0561 | .00381 | .00345 | .00040 | .0515 |
| | .00281 | .0694 | .00703 | .00445 | .00080 | .0561 |
| | .00450 | .0731 | | | .0012 | .0593 |
| | | | | | .0030 | .0676 |
| | | | | | .0052 | .0710 |
| | | | | | .0068 | .0725 |
| 28 | $1.7 \times 10^{-5}$ | 0.0226 | | | $1.7 \times 10^{-5}$ | .0226 |
| | 0.00104 | .0625 | | | 0.0008 | .0576 |
| | .00257 | .0707 | | | .0012 | .0609 |
| | .00508 | .0765 | | | .0020 | .0655 |
| | .00751 | .0800 | | | .0040 | .0720 |
| | | | | | .0072 | .0750 |
| 25 | .000015 | .00746 | | | .000015 | .00746 |
| | .000037 | .0181 | | | .00037 | .0181 |
| | .000333 | .0376 | | | .0002 | .0315 |
| | .000898 | .0477 | | | .0004 | .0380 |
| | .00160 | .0528 | | | .001 | .0465 |
| | .00460 | .0629 | | | .002 | .0525 |
| | | | | | .004 | .0585 |
| | | | | | .006 | .0612 |
| | | | | | .007 | .0625 |

## Discussion

The data in the foregoing tables can be represented accurately by the simple Langmuir equation (1). The saturation value for the adsorption corresponds to 33% of the surface covered. This was calculated from the number of molecules required to form a complete monomolecular film as estimated from the diameter of the acetone molecule.[24] The adsorbed layer is therefore not greater than one molecule in thickness, in agreement with the work of Carver,[25] Frazer, Patrick and Smith,[26] Latham,[27] *et al.*, for the adsorption of vapors on plane surfaces. Up to pressures of one-thousandth of the saturation pressure of acetone, no evidence for capillary condensation was obtained.

In conclusion, the author wishes to express his appreciation to Professor W. E. Garner, who suggested this study and under whose direction it was

[24] Landolt-Börnstein, Vol. I, pp. 120, 122.

[25] Carver, THIS JOURNAL, **45**, 63 (1923).

[26] Frazer, Patrick and Smith, *J. Phys. Chem.*, **31**, 847 (1927).

[27] Latham, THIS JOURNAL, **50**, 2996 (1928).

carried out, and to the Imperial Chemical Industries, Limited, for a personal grant.

## Summary

1. The adsorption of carbon monoxide, oxygen and argon by mica surfaces has been measured from pressures $1 \times 10^{-4}$ cm. to $2 \times 10^{-2}$ cm., and at temperatures 90°A. and 193°A.

2. The data for the adsorption of carbon monoxide and oxygen at 90°A. are adequately represented by the Langmuir formula. No simple equation expresses the results for argon.

3. The isotherms at 193°A. are linear for small amounts adsorbed and up to pressure $8 \times 10^{-3}$ cm. The Langmuir equation is followed at higher pressures.

4. The magnitude of the adsorption has been shown to be dependent upon the conditions of the outgassing of the surface. A suggested explanation is based on the concept of the activation energy for adsorption processes as postulated by Taylor.

5. The thickness of the adsorbed film of carbon monoxide, oxygen and argon, is not greater than unimolecular.

6. The adsorption of acetone vapor on mica at room temperature has also been measured. The data are accurately represented by the Langmuir equation. The adsorbed layer is not greater than one molecule in thickness.

BRISTOL, ENGLAND

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

# THE QUANTITATIVE SEPARATION OF GERMANIUM AND ARSENIC[1]

BY HAROLD J. ABRAHAMS AND JOHN HUGHES MÜLLER

RECEIVED AUGUST 1, 1931 PUBLISHED JANUARY 7, 1932

The quantitative separation of germanium from arsenic is attended by considerable difficulty, a fact which is not surprising in view of their relative positions in the periodic arrangement of the elements. As these two elements are so universally associated in germanium bearing minerals, this separation has been made the subject of several investigations in the past. As early as 1886 Winkler[2] suggested a means of effecting this separation through the mixed sulfides. According to this method, both elements are taken into alkaline solution as thio compounds, and the

[1] From the thesis presented by Harold J. Abrahams to the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Winkler, *J. prakt. Chem.*, **142**, 194 (1886).

solution neutralized with acid, a slight excess of acid then being added to bring about complete reprecipitation of the arsenic sulfide. This method depends upon the existence of a soluble alkali thiogermanate and the stability of hypothetical thiogermanic acid in a solution, the hydrogen-ion concentration of which is sufficient to decompose the thioarsenite quantitatively. The arsenic sulfide thus formed is removed by filtration, and the germanium is recovered from the filtrate. Truchot[3] mentions the same separation. No analytical data are given by either author.

Dennis and Papish[4] have described a method for the preparation of pure germanium tetrachloride from a mixture containing arsenic and germanium by distilling the mixture with hydrochloric acid in a current of chlorine. The pentavalent arsenic which results is completely non-volatile under the conditions of this process. Dennis and Johnson,[5] who have investigated this excellent means of separating arsenic from germanium, state that, if their column still is used, 83% of the germanium is obtained in the first distillation, and 16% from the residue by later runs.

Various modifications[6] of this method have appeared in which strong oxidizing agents, such as potassium dichromate, etc., have been added to the hydrochloric acid to maintain arsenic in the pentavalent condition.

A separation based upon the failure of germanium sulfide to precipitate in the presence of hydrofluoric acid has been proposed by Müller.[7] In this method the separation of germanium and arsenic proceeds without difficulty, but the recovery of germanium in a weighable form from the very stable fluogermanic acid is difficult.

The purpose of the present investigation was to study a separation based upon the selective precipitation of arsenic, by hydrogen sulfide, from solutions containing both elements in the presence of a controlled amount of free acid.

## Preliminary Experiments

It is a well known fact that germanium sulfide separates practically completely from an aqueous solution of the dioxide when treated with hydrogen sulfide, if the hydrogen-ion concentration is sufficiently high. Concerning the mechanism of this reaction, it is believed that, in the presence of sufficient acid, germanic cations reach a concentration which permits precipitation of germanium sulfide. In the absence of the limiting hydrogen-ion concentration, however, hydrogen sulfide is entirely without effect on such a solution over many hours. To determine the limiting value of acidity necessary for the first separation of germanium sulfide, the

[3] Truchot, "Les Terres Rares," Paris, **1898.**

[4] Dennis and Papish, THIS JOURNAL, **43,** 2131 (1921).

[5] Dennis and Johnson, *ibid.*, **45,** 1380 (1923).

[6] Browning and Scott, *Am. J. Sci.*, **46,** 663 (1918).

[7] Müller, THIS JOURNAL, **43,** 2549 (1921).

experiments shown in Table I were made. Sulfuric acid was used as the free acid because small amounts of this acid retained in the precipitated germanic sulfide did not interfere with the ultimate conversion to dioxide.

**Experiments 1a to 12c Inclusive.**—Table I shows in brief the effect of

TABLE I

PRELIMINARY EXPERIMENTS. EFFECT OF HYDROGEN SULFIDE ON GERMANIC OXIDE SOLUTIONS UNDER VARYING ACID CONCENTRATION

| No. | Vol., cc. | $GeO_2$, mg. | $As_2O_3$, mg. | Final acid normality | Hours | Results | Remarks |
|---|---|---|---|---|---|---|---|
| 1a | 52.2 | 250 | .. | 0.008 | 16 | Faint turbidity | Turbidity, sulfur; no $GeS_2$ |
| 1b | 52.2 | 25 | .. | .008 | 16 | Clear | |
| 2a | 54.4 | 250 | .. | .016 | 18 | Faint turbidity | Turbidity—sulfur |
| 2b | 54.4 | 25 | .. | .016 | 18 | Unchanged | |
| 3a | 56.4 | 250 | .. | .023 | .. | Faint turbidity | 1 g. $(NH_4)_2SO_4$ added |
| 3b | 56.4 | 25 | .. | .023 | .. | Unchanged | |
| 4a | 57.5 | 250 | .. | .026 | 19 | Faint turbidity | |
| 4b | 57.5 | 25 | .. | .026 | 19 | Unchanged | |
| 5a | 58.7 | 250 | .. | .030 | 20 | Faint turbidity | |
| 5b | 58.7 | 25 | .. | .030 | 20 | Unchanged | |
| 6a | 60.7 | 250 | .. | .035 | 21 | Faint turbidity | |
| 6b | 60.7 | 25 | .. | .035 | 21 | Unchanged | |
| 7a | 62.9 | 250 | .. | .041 | 21.5 | Faint turbidity | |
| 7b | 62.9 | 25 | .. | .041 | 21.5 | Unchanged | |
| 8a | 65.1 | 250 | .. | .046 | 22 | Faint turbidity | |
| 8b | 65.1 | 25 | .. | .046 | 22 | Unchanged | |
| 9a | 67.3 | 250 | .. | .051 | 23 | Faint turbidity | |
| 10a | 50.0 | 125 | .. | 1.0 | 5 min. | Heavy ppt. | Dense ppt. ($GeS_2$) overnight |
| 10b | 50.0 | 125 | .. | 0.5 | 10 min. | Heavy ppt. | |
| 10c | 50.0 | 125 | .. | .25 | 2 | Little ppt. | |
| 10d | 50.0 | 125 | .. | .125 | 2 | Turbid | |
| 11 | 50.0 | 125 | .. | .09 | 48 | Unchanged | |
| 12a | 50.0 | 125 | .. | .1 (HCl) | 48 | Faint turbidity | 1 g. $NH_4Cl$ added |
| 12b | 50.0 | 125 | .. | .05(HCl) | 48 | Unchanged | 1 g. $NH_4Cl$ added |
| 12c | 50.0 | 125 | .. | .025(HCl) | 48 | Unchanged | 1 g. $NH_4Cl$ added |
| 13a | 50.0 | ... | 31 | .. | 24 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added |
| 13b | 50.0 | ... | 31 | .004 | 24 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added. |
| 13c | 50.0 | ... | 31 | .008 | 24 | $As_2S_3$ pptd. | Ppt. more satisfactory than in a |
| 13d | 50.0 | ... | 31 | .. | 24 | $As_2S_3$ colloidal | |
| 13e | 50.0 | ... | 1 | .. | 24 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added |
| 13f | 50.0 | ... | 1 | .004 | 24 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added |
| 14a | 50.0 | 10 | 1 | .004 | 16 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added |
| 14b | 50.0 | 50 | 1 | .004 | 16 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added |
| 14c | 50.0 | 125 | 1 | .004 | 16 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added |
| 15a | 77.0 | 375 | 0.5 | .004 | 1 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added |
| 15b | 77.0 | 375 | 1 | .004 | 1 | $As_2S_3$ pptd. | 1 g. $(NH_4)_2SO_4$ added |
| 16a | 92.2 | 375 | 1 | .033 | 3 | $As_2S_3$ did not settle | Ppt. completely removed by filtration. Filtrate gave snow-white $GeS_2$ |
| 16b | 92.1 | 375 | 0.5 | .033 | 16 | $As_2S_3$ did not settle | |
| 16c | 92.2 | 250 | 1 | .032 | 3 | $As_2S_3$ did not settle | |
| 16d | 117.1 | 375 | 0.5 | .068 | 16 | $As_2S_3$ did not settle | |
| 16e | 124.4 | 500 | 1 | .032 | 3 | $As_2S_3$ did not settle | |

hydrogen sulfide upon solutions of pure germanium dioxide, under varying conditions of free acid concentration. These results indicate that no precipitation of germanium sulfide takes place until the acid concentration exceeds 0.09 *N*.

In all experiments it was necessary to add 1 g. of ammonium sulfate as suitable electrolyte in order to prevent colloidal dispersion of any arsenic sulfide, under existing conditions of low acid concentration. Preliminary experiments indicated that the presence or absence of ammonium sulfate had no effect upon the action of hydrogen sulfide in the case of solutions containing only germanium dioxide. It may be noted that sulfuric acid was used throughout as the free acid and ammonium sulfate as electrolyte, because, unlike hydrochloric acid and its corresponding salt, these reagents could not form any volatile germanium compound.

Experiments 12a, b and c indicate that free hydrochloric acid and ammonium chloride may be substituted for sulfuric acid and ammonium sulfate without any observable change in precipitation effect, but chlorides were purposely avoided in quantitative work for reasons given above.

Experiments 13a to 13f concern the effect of hydrogen sulfide on solutions containing arsenic in absence of germanium.

Experiments 14a, b and c were duplications of 13e and f with the exception that they contained approximately 10, 50 and 125 mg. of germanium dioxide in addition. They were saturated with hydrogen sulfide overnight, whereupon all arsenious sulfide was found at the bottom of the flask in a granular condition. The volume of the precipitated arsenious sulfide, on comparison with a standard, seemed to indicate little or no removal of germanium. This behavior was given a more rigorous test by setting up experiments 15a and b: 15a contained 0.5 mg. of arsenious oxide, 1 g. of ammonium sulfate, 1.5 cc. of 0.2 *N* sulfuric acid, and 375 mg. of germanium dioxide (total volume 77 cc.); 15b contained 1 mg. of arsenious oxide but was otherwise identical with 15a. On saturating with hydrogen sulfide, finely divided but filterable arsenious sulfide appeared in each case. Expts. 16a to e, with mixtures of the two oxides, in the ratios of 1 arsenious oxide to 375 germanium dioxide, and 1 arsenious oxide to 750 germanium dioxide, were then made. These solutions contained 1 g. of ammonium sulfate and varied in acid concentration from 0.03 to 0.06 *N*. While the arsenious sulfide in these experiments did not settle, it could be removed perfectly by filtration. The germanium sulfide precipitated in the filtrate was snow white. (The limit of acidity for the non-precipitation of germanium is 0.09 *N*, as shown by experiments 10 and 11.)

## Quantitative Analysis of Mixtures

The investigation was now made quantitative by making mixtures of known concentrations and analyzing them in the light of the knowledge gained from the experiments discussed above. Mixtures each containing 242 mg. of germanium dioxide but

varying in arsenious oxide content from 50 to 1.1 mg. and one mixture containing 484 mg. of germanium dioxide to 1.1 mg. of arsenious oxide were made. They were then analyzed by the following procedure. To the mixtures measuring 60 to 70 cc., 3 cc. of approximately 0.1 *N* sulfuric acid and 1 g. of ammonium sulfate were added and the mixtures saturated with hydrogen sulfide in a closed system under pressure. The arsenic sulfide was filtered off, washed thoroughly with hydrogen sulfide water containing ammonium sulfate, and determined as magnesium pyroarsenate, by dissolving in the minimum amount of ammonia, oxidizing with hydrogen peroxide, boiling to destroy the excess of the latter, and then following the recommendation of McNabb.[8]

The filtrate from the arsenic sulfide was made 6 *N* with sulfuric acid and the germanium sulfide precipitated in the usual way. The sulfide was filtered upon a small glass filtering crucible (capacity about 15 cc.). A part of the filtrate was resaturated with hydrogen sulfide, while the rest of the filtration was being carried out. This solution was used in removing any precipitate adhering to the precipitation flask. The precipitate was sucked down as dry as possible and washed with a few cc. of 2 to 3 *N* sulfuric acid saturated with hydrogen sulfide.

The germanium was determined by hydrolytic conversion of the sulfide to dioxide as follows. The small glass filter containing the sulfide was introduced into a weighed quartz beaker containing enough boiling water to cover completely the filter crucible and its contents. The water was kept actively boiling and a cover glass was used to exclude air as far as possible. This is necessary to prevent oxidation of escaping hydrogen sulfide and consequent separation of free sulfur. Boiling was continued until the whole of the precipitate had passed into clear solution, indicating completion of the hydrolysis of the sulfide. The glass filter crucible was now removed and washed free of adhering solution. At this point the weighed quartz beaker contained nothing but germanic oxide solution and perhaps traces of free sulfur. Evaporation was continued to near dryness, at which stage a small amount of pure nitric acid was added, and evaporation then continued to complete dryness. The dioxide resulted upon ignition.

It was noted that several treatments with nitric acid were required in case of accidental separation of appreciable amounts of free sulfur, but complete exclusion of air, especially during the initial hydrolysis of the sulfide, or in its precipitation made this unnecessary.[9]

TABLE II

QUANTITATIVE SEPARATION OF GERMANIUM AND ARSENIC

| | $As_2O_3$ taken, g. | Found, g. | $GeO_2$ taken, g. | Found, g. |
|---|---|---|---|---|
| 1 | 0.0500 | 0.0498 | 0.2417 | 0.2412 |
| 2 | .0500 | .0503 | | |
| 3 | .0250 | .0249 | .2417 | .2413 |
| 4 | .0250 | .0251 | | |
| 5 | .0125 | .0125 | .2417 | .2415 |
| 6 | .0125 | .0125 | | |
| 7 | .0062 | .0064 | .2417 | .2420 |
| 8 | .0011 | .0013 | .2417 | .2415 |
| 9 | .0011 | .0008 | .4840 | .4834 |

Table II shows clearly that the described separation of germanium and arsenic is satisfactory for mixtures containing large amounts of germanium

[8] McNabb, THIS JOURNAL, **49**, 1451 (1927).

[9] A detailed study of the hydrolytic conversion of germanium sulfide to germanium dioxide will appear in a separate paper by Müller and Eisner, *Ind. Eng. Chem., Anal. Ed.*, January, 1932.

and small amounts of arsenic, and that the separation can be effected in a single operation.

From all the qualitative and quantitative experiments with mixtures of arsenic and germanium sulfides, it was observed that very small amounts of arsenic show an unexpected tinctorial effect upon the snow-white germanic sulfide. It is of interest to investigate the minimum amount of arsenic sulfide which would produce an observable effect on the appearance of germanium sulfide. To this end four standards were made, each containing 121 mg. of germanium dioxide, 1 g. of ammonium sulfate and 4.5 cc. of concentrated sulfuric acid, the total volume of each being about 30 cc. Mixture (a) contained 0.28 mg. of arsenious oxide in addition, mixture (b) 0.17 mg. of arsenious oxide, mixture (c) 0.11 mg. of arsenious oxide, and mixture (d) 0.06 mg. These standard mixtures were saturated with hydrogen sulfide: (a) and (b) showed a distinct yellowness, (c) and (d) appeared yellow by comparison with a white surface, or standard precipitate of pure germanic sulfide. From the above it is seen that any quantity of arsenic contaminating the germanium in excess of about 0.2% will be observable by simple inspection.

Mixtures containing large amounts of arsenic and small amounts of germanium and mixtures of equal quantities of both elements were next investigated.

Three mixtures of approximately the same germanium dioxide and arsenious oxide content were made—A, B and C. "A" contained 242 mg. of germanium dioxide, 250 mg. of arsenious oxide, 2 g. of ammonium sulfate and 1 cc. of *N* sulfuric acid (total volume of 103 cc.). B was identical with A, but was further diluted with 50 cc. of water (the total volume being 153 cc.). C was identical with B. All were saturated with hydrogen sulfide for two hours. C was raised to almost boiling and so maintained while the gas was bubbled through. Experiment B afforded an opportunity to observe any advantage due to greater dilution. The results obtained were poor, as A, containing 242 mg. of germanium dioxide, permitted the recovery of but 232.6 mg. B and C were correspondingly low by approximately 6 mg.

It was probable that the large volume of the arsenic sulfide prevented thorough removal of germanium dioxide solution during the washing process in experiments A, B and C. The analyses were therefore repeated with one-half the quantity of each oxide, though the total volume remained at 150 cc. The quantity of *N* acid was reduced to 0.5 cc. and the precipitates were washed by decantation. "C," as previously, was saturated at elevated temperature. Results are shown in Table III.

Removal of any germanium sulfide present in the arsenious sulfide next suggested itself. Mixtures of the oxides were made, diluted to 150 cc. and 1 g. of ammonium sulfate and 0.5 cc. of *N* sulfuric acid added. The mix-

TABLE III

EXPERIMENTAL RESULTS

| | $GeO_2$ taken, g. | Found, g. | $As_2O_3$ taken, g. | Found, g. |
|---|---|---|---|---|
| A | 0.1210 | 0.1200 | 0.1250 | 0.1260 |
| B | .1210 | .1201 | .1250 | .1261 |
| C | .1210 | .1215 | .1250 | .1255 |

tures were saturated with hydrogen sulfide and the precipitates washed by decantation. These precipitates, consisting of arsenic sulfide containing traces of germanic sulfide, were redissolved in a minimum quantity of ammonia (1:2) and the solution diluted to about 150 cc. *N* sulfuric acid was then carefully added, with constant stirring, until the solution was neutral, then enough excess acid to make the medium between 0.05 and 0.1 *N*. This procedure is a modification of the old method originated by Winkler and mentioned by Truchot and depends upon the relative stability of hypothetical thiogermanic acid. The mixture was saturated with hydrogen sulfide and filtered. This small amount of germanium dioxide held by the arsenious sulfide is evidently quantitatively recoverable, as shown in Table IV. The germanium dioxide in the filtrate was determined separately in order to learn the amount of the germanium sulfide held by the arsenic sulfide. Results are shown in Table IV.

TABLE IV

EXPERIMENTAL RESULTS

| | $GeO_2$ taken, g. | Found, g. | $As_2O_3$ taken, g. | Found, g. |
|---|---|---|---|---|
| 1 | 0.1210 | 0.1205 | 0.1250 | 0.1252 |
| 2 | .1210 | .1206 | .1250 | .1247 |
| 3 | | | .1250 | .1254 |

The germanium dioxide removed from the arsenious sulfide was found to weigh 0.3 mg.

Analysis was then made of mixtures containing 125 mg. of arsenious oxide and amounts of germanium dioxide varying from 1.3 to 60.5 mg., with the results given in Table V.

TABLE V

EXPERIMENTAL RESULTS

| | $GeO_2$ taken, g. | Found, g. | $As_2O_3$ taken, g. | Found, g. |
|---|---|---|---|---|
| 1 | 0.0012 | 0.0013 | 0.1250 | 0.1250 |
| 2 | .0062 | .0066 | .1250 | .1254 |
| 3 | .0120 | .0122 | .1250 | .1254 |
| 4 | .0302 | .0299 | .1250 | .1249 |
| 5 | .0605 | .0602 | .1250 | .1250 |

The germanium dioxide contents of Nos. 1, 2 and 3 were determined by dissolving germanium sulfide in ammonia, collecting in a weighed crucible, oxidizing with a few drops of hydrogen peroxide, evaporating and carefully igniting. This procedure was followed because the quantities were small.

For the estimation of the larger quantities of germanium dioxide, the method of hydrolytic conversion to oxide was used.

From final results as shown in Table V, it may be concluded that higher dilution of the solution of the mixtures containing relatively large amounts of arsenic favors the more complete separation of these elements (see Table IV). Further treatment of the precipitated arsenic sulfide as described is necessary if the arsenic exceeds 15–20% in the mixture.

As all of the above described separations have dealt with simple mixtures of the pure oxides of germanium and arsenic, it was thought advisable to extend this method of separation to a naturally occurring arsenical germanium compound. Germanite was selected for this purpose because its composition is of special interest and only a few analyses of this mineral have been heretofore reported.[10]

## Analysis of Germanite

A carefully selected sample of germanite which was free from any visible occluded mineral was analyzed for total constituents, making use of the method herein described for the separation and determination of arsenic and germanium.

A 3-g. sample of the finely divided mineral was oxidized by repeated evaporation with nitric acid in the presence of sulfuric acid, and the opened-up material thus obtained was treated with a large excess of hydrochloric acid. Distillation was carried out until all germanium and much of the arsenic had been collected in the acid distillate. The latter was analyzed as described. The following results were obtained by total analysis.

| | | | |
|---|---|---|---|
| Ge | 7.37 | Zn | 2.87 |
| As | 3.92 | Pb | 0.71 |
| Cu | 45.38 | S | 30.96 |
| Fe | 5.89 | W | 0.10 |
| $Ga_2O_3$ | 0.68 | Gangue | 1.47 |
| $Al_2O_3$ | 0.13 | Total | 99.48 |

Recalculation of these values on the assumption that the small amounts of aluminum, gallium, zinc, lead, arsenic, tungsten and siliceous gangue are independent constituents indicates the probable composition of this mineral to be $7CuS \cdot FeS \cdot GeS_2$.

## Summary and Conclusions

1. Germanium and arsenic are shown to be quantitatively separable by a simple precipitation of the sulfides, under regulated conditions of free acid concentration.

[10] Pufahl, *Metall u. Erz*, **19**, 324 (1922); Kriesel, *ibid.*, **20**, 357 (1923); *Chem.-Ztg.*, **48**, 961 (1924); Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924); Todd, *Min. Toronto Studies*, **17**, 62 (1924).

2. Small amounts of arsenic can be removed completely from large quantities of germanium in a single operation. Relatively large quantities of arsenic require a retreatment of the precipitated sulfide to recover traces of occluded or co-precipitated germanium sulfide.

3. Very small quantities of arsenic sulfide are shown to have marked coloring effect upon pure white germanium sulfide. This coloring effect is quantitatively studied.

4. Complete analysis of a selected sample of the mineral germanite is appended.

PHILADELPHIA, PENNSYLVANIA

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

# THE PHOTOCHEMICAL POLYMERIZATION OF ACETYLENE

BY S. C. LIND AND ROBERT LIVINGSTON

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## Introduction

In an earlier paper[1] one of us pointed out the interest attaching to the comparison of the yields of chemical action per quantum and per ion pair in various reactions. A few rough comparisons were possible with data existing in the literature, but it appeared preferable to select some suitable reactions which could be investigated photochemically and with alpha rays under the best experimental conditions.

The reactions that have been chosen are the polymerization of acetylene and of some of its simpler derivatives. As expected, the alpha-ray reactions yielded readily to quantitative investigation and the results from six gaseous unsaturates have been recently published.[2]

The following deals with the photochemical yield in the polymerization of acetylene, of which a preliminary report has already been made.[3]

Acetylene polymerization has the advantage of being a direct reaction from gas to solid with no known side reactions or gaseous products. The relatively high yield is favorable for manometric work. In the photochemical reaction the one complication, the fogging of the window transmitting ultraviolet by deposition of the solid polymer, has been overcome by making measurements with a minimal amount of reaction, which is rendered possible by the employment of a very sensitive differential gage.

The photochemical condensation of acetylene, which was first reported by Berthelot and Gaudechon,[4] has been qualitatively studied by Bates

[1] Lind, *J. Phys. Chem.*, **32**, 575 (1923); "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., New York, **1928**, p. 215.

[2] G. B. Heisig, THIS JOURNAL, **53**, 3245 (1931).

[3] Lind and Livingston, *ibid.*, **52**, 4613 (1930).

[4] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

and Taylor[5] and by Reinke.[6] It was demonstrated by these investigators that acetylene is polymerized to a yellowish inert solid, presumably cuprene, when it is exposed to the complete radiation of a quartz mercury arc. Reinke showed by the use of a glass filter that the reaction was not caused by light of wave length longer than 3000 Å. Extreme purification had no appreciable effect on the course of the reaction. In both of these investigations, the acetylene contained some mercury vapor, the latter two authors assuming that, since a "hot arc" was used, no resonance light which could be absorbed by the cold mercury vapor was produced.

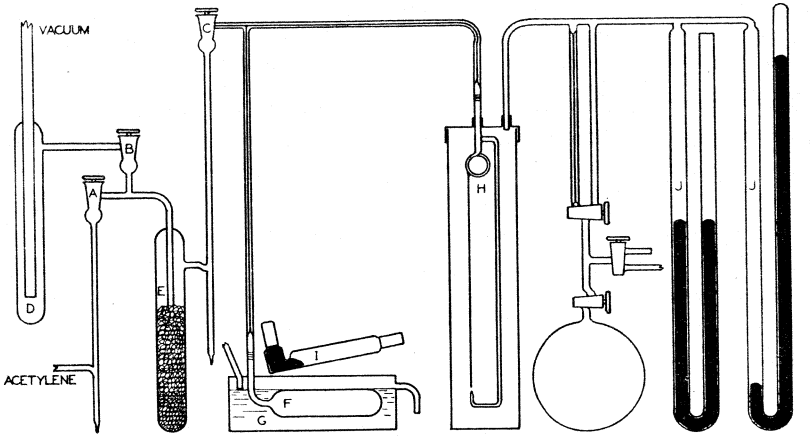


Fig. 1.—Apparatus.

## Effect of Pressure and Temperature

**Apparatus.**—In the experiments presented in this paper, a hot arc was used and particular care was taken to prevent the contamination of the acetylene by mercury vapor. The acetylene was taken from a commercial cylinder (solution in acetone). It was passed through a series of wash bottles containing sodium bisulfite solution, concentrated sulfuric acid saturated with potassium dichromate and sodium hydroxide solution. In some of the experiments an extra bottle containing a solution of copper sulfate in sulfuric acid was included in the train. The gas then passed through a column of glass wool, to remove spray, and was condensed with liquid air. It was then fractionated at low temperature, to remove permanent gases, and was stored in a large flask over fused potassium hydroxide.

The reaction system, represented in Fig. 1, was isolated from the storage vessel by stopcock A. The system was evacuated through stopcock B, which was only opened when the trap D was surrounded by liquid air. A mercury diffusion pump was used and the apparatus was always evacuated to a pressure less than $10^{-4}$ mm. of mercury before the acetylene was admitted.[7] Before being admitted to the reaction chamber an excess of acetylene was frozen, by means of liquid air, in trap E, which was filled with

[5] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

[6] Reinke, *Z. angew. Chem.*, **41**, 1144 (1928).

[7] In some of the earlier experiments, an oil pump only was used, and the system was flushed out with acetylene several times before beginning the experiment.

(dental) gold foil. The liquid air was then removed and the acetylene was allowed to evaporate into the reaction system until the desired pressure had been reached; stopcock C was then closed. Stopcocks A, B and C were lubricated with a mixture of ortho and metaphosphoric acids,[8] during the majority of the experiments; however, in several experiments ordinary vacuum stopcock grease was substituted without apparently affecting the results. The reaction vessel F is a quartz cylinder, 3.4 cm. in diameter and 15 cm. long, connected to the system by a graded seal. The temperature of the vessel was controlled by means of a flowing water-bath G. The pressure was measured with a quartz spiral manometer H,[9] which was used as a null instrument; it was connected to the system by a graded seal. The balancing pressure was measured with a mercury manometer which was read with an accurate cathetometer. The pressure readings were reproducible within 0.2 mm. The light source was a Cooper–Hewitt horizontal quartz mercury arc (I) operating at 42 volts and 4.2 amps. The arc was placed parallel to the reaction vessel and about 5 cm. above it.

**The Reaction Product.**—When acetylene is illuminated under these experimental conditions, the pressure decreases gradually and a yellowish solid, apparently cuprene, forms in the reaction vessel. The cuprene is largely deposited on the bottom of the vessel; however, a thin film forms on the upper surface, through which the light is entering. The experiments showed that this film does not affect the rate of the reaction appreciably until the pressure has been reduced by about 3 mm.; when the pressure has been reduced by 10 mm., the reaction rate falls to about a quarter of its initial value.

After two of the experiments, the gas was tested for hydrogen by condensing the acetylene with liquid air; if there was any residual pressure, it was less than 0.2 mm., the limit of sensitivity of the manometer. To determine whether ultraviolet light has any effect on cuprene, the reaction system was evacuated after one experiment, and the film of cuprene was exposed to the radiation of the arc for several hours. The solid did not change in color, nor was there any measurable pressure of gas produced. When heated in a vacuum, the cuprene darkened, but did not sublime. The deposit was easily and completely removed from the reaction vessel by admitting air to it and heating it with a hand torch.

**Effect of Pressure.**—Six experiments were performed at pressures ranging from 2.6 to 65.0 cm. These experiments are summarized in Table I. The values of the initial pressure and the average temperature are given in the first and second columns, respectively. The observed values of the initial rate, in centimeters per minute, are given in the third column.

To eliminate the uncertainties introduced by the film of cuprene, the values of the initial rate are based upon the first 2 mm. fall in pressure.

[8] Stephens, THIS JOURNAL, **52,** 635 (1930). The lubricant recommended by Boughton, *ibid.*, **52,** 2813 (1930), was also tried, but was found to have too high a vapor pressure for use in a vacuum system.

[9] Bodenstein and Dux, *Z. physik. Chem.*, **85,** 300 (1913).

TABLE I

RATE OF POLYMERIZATION AS A FUNCTION OF PRESSURE

| $P_0$, cm. | $t$, °C. | $V$(measured) |
|---|---|---|
| 64.5 | 11.0 | 0.042 |
| 43.5 | 13.5 | .033 |
| 33.3 | 12.0 | .032 |
| 8.8 | 13.0 | .013 |
| 7.2 | 11.7 | .013 |
| 2.7 | 11.4 | .0035 |

To illustrate the type of pressure–time curve obtained, the detailed results of several experiments are plotted in Fig. 2. Since the temperature of the flowing water-bath sometimes varied by so much as 1.5°, it was necessary to correct the observed pressures to a constant (average) temperature, by means of the perfect gas laws. The volumes of the quartz spiral and the capillary corrections were sufficiently small to render the effect of fluctuations in room temperature negligible.

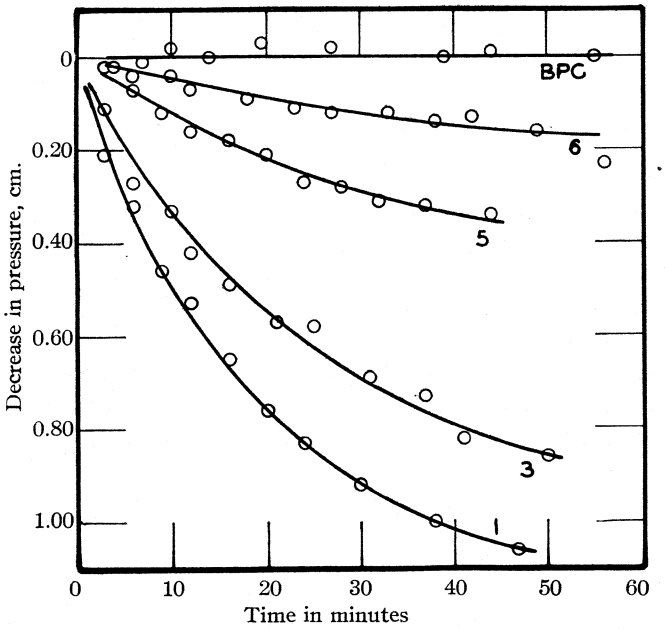


Fig. 2.—Rate of polymerization.

The data of Table I indicate that for the lower pressures the rate is practically proportional to the pressure, but at higher pressures it approaches a constant value. The simplest explanation of this result is that the rate is directly proportional to the intensity of the absorbed light, but is otherwise independent of the pressure of the acetylene. This may be demonstrated more definitely by combining the data of Table I with

the results of the absorption measurements which are given in Fig. 6. In order to use the absorption measurements for this purpose, it is necessary to assume (as a first approximation) that the energy distribution of the absorbable light produced by the optical system used in those experiments is the same as that of the horizontal arc used in the rate measurements. If this may be taken as true, the percentage of absorption in the two sets of experiments will, for any given pressure, differ by a constant multiplier, $c$.

$$\left(\frac{I_{\text{abs.}}}{I_0}\right)_{\text{rate}} = C\left(\frac{I_{\text{abs.}}}{I_0}\right)_{\text{absorb.}}$$

Since $(I_0)_{\text{rate}}$ was maintained constant

$$(I_{\text{abs.}})_{\text{rate}} = C'\left(\frac{I_{\text{abs.}}}{I_0}\right)_{\text{absorb.}}$$

Since we have already assumed that the rate is proportional to the intensity of the light absorbed

$$V = k\,(I_{\text{abs.}})_{\text{rate}}$$

we may write

$$V = kC'\left(\frac{I_{\text{abs.}}}{I_0}\right)_{\text{absorb.}}$$

or

$$\log V = \log (kC') + \log \left(\frac{I_{\text{abs.}}}{I_0}\right)_{\text{absorb.}}.$$

This relation may be tested by plotting the logarithm of the rate against the pressure, and then plotting the logarithm of the percentage absorption against pressure on the same graph to the same scale. If the relation holds, the two curves will differ only by a constant factor in the logarithmic scale. In Fig. 3 a suitable constant factor has been added to each value of the logarithm of the percentage absorption to make the two curves coincide in the region of higher pressures. It is apparent that the results are in definite agreement with the prediction, and afford ample justification for the statement that the rate is proportional to the intensity of the light absorbed and is otherwise independent of the pressure of the acetylene. The small departure which is noticeable in the region of low pressures is very probably due to the difference in the light sources.

**Effect of Temperature.**—To determine the effect of temperature, two experiments were performed at 39° and at 10 cm. pressure. The initial rates of these experiments were 0.029 and 0.024. Using the average of these values and a 10-cm. value obtained by graphical interpolation of the 12° measurements, it may be shown that the 10° temperature coefficient

$$\log K_{10} = \frac{10}{39 - 12} \log \frac{V_{39}}{V_{12}}$$

has a value of 1.25. It is possible that this observed temperature coefficient may be due in part to the temperature coefficient of the absorption of light. However, an attempt to measure the temperature coefficient

of the absorption using a thermopile, galvanometer, and a light source which is described later in this paper, indicated that the absorption was practically constant over this temperature range. While this attempt to measure the temperature coefficient of the absorption was admittedly crude, it seems very probable that the value 1.25 is that of the temperature coefficient of the photochemical reaction itself. This is in interesting contrast with the radiochemical reaction, the ion pair yield of which is independent of the temperature from 0° to 100°.[10]

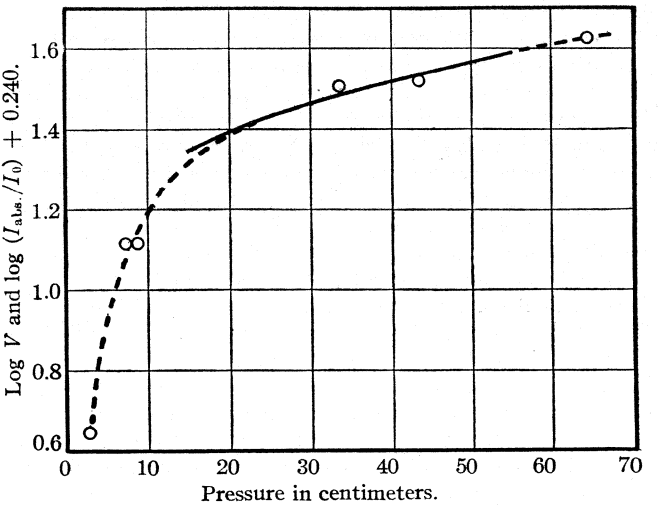


Fig. 3.—Reaction rate and the percentage absorption of light: ——, absorption; -O-O-, rate.

**Photochemical Threshold.**—Reinke showed that the light transmitted by a lead glass filter, having a sharp transmission limit at about 3000 Å., was not capable of causing the polymerization of acetylene. This work has been extended in the present investigation by using several of the Corning ultraviolet transmitting glasses. None of these, not even a new 4.8 mμ plate of the comparatively transparent blue-purple corex, was capable of transmitting an appreciable amount of photochemically active light. The experiments with blue-purple corex were performed with acetylene at 10 cm. pressure, both at 12 and 41°. The results of the measurements at 41° are represented by the points labeled BPC on Fig. 2. A series of spectrograms of the mercury arc taken with and without this filter indicates that an appreciable fraction of 2537 Å. is transmitted by it.[11] We may conclude from this that light of wave lengths equal to or

[10] See Mund and Koch, *J. Phys. Chem.*, **30**, 292 (1926); Lind and Bardwell, THIS JOURNAL, **48**, 1556 (1926).

[11] The data of Anderson, Fraser and Bird, *J. Optical Soc.*, **17**, 458 (1928), indicate that even an *aged* purple corex filter transmits 2% of λ2537 and 1% of λ2480 Å.

greater than λ2537 Å. are either not absorbed or are photochemically inefficient. This question will be discussed in a later section of this paper.[3]

## Determination of the Quantum Yield

**Apparatus.**—Certain modifications of the apparatus, represented by Fig. 1, were necessary for the quantum yield measurements. A quartz cylinder with fused on plane ends was substituted for the reaction vessel used in the earlier experiments. It was 2.8 cm. in diameter and 4.7 cm. long.

It was necessary to use a light source of such a character that a measurable amount of the radiation would be absorbed by acetylene. A high pressure capillary arc of the type described by Langer and Meggers[12] was used. The arc consists of a thick-walled horizontal quartz capillary, 1.5 mm. inside diameter and 5 cm. long, connected to two vertical tubes open at the top. Constrictions were made in the vertical tubes about a centimeter above the points where they joined capillary, and close-fitting iron electrodes were introduced through these constrictions. The capillary and side tubes were filled with carefully purified mercury,[13] which was boiled in place to expel any trapped air. The arc was started by heating a point on the capillary with a blast lamp. As soon as the arc struck it was plunged into a copper tank through which distilled water was flowing. The capillary of the arc was placed directly behind a quartz window in the side of the tank. A diaphragm with a 1.5-mm. circular hole was fastened to the front face of the window. The arc was operated at 60 volts and 3.2 amperes. The intensity of the light, particularly of the shorter ultraviolet, is diminished fairly rapidly by a brownish film which forms on the inside of the capillary. However, this deposit can be easily and completely removed with dilute hydrofluoric acid.

The shorter ultraviolet radiation of the arc was isolated by means of a focal isolation apparatus.[14] This device utilizes the chromatic aberration of a quartz lens to separate the extreme ultraviolet from the visible and near ultraviolet. Two spherical fused quartz lenses were arranged to project a slightly converging beam of light through the reaction cell. The central part of the first lens was blocked out with a circular opaque screen, and a diaphragm was placed at its focus for λ2300 Å. to intercept all but the shorter wave lengths. A series of spectrograms indicated that the emergent light does not contain more than 2 or 3% of light of wave length greater than 2537 Å. and that the intensity of λ2537 Å. is considerably diminished relative to the shorter wave lengths. The system absorbs practically all light of wave lengths less than 2054 Å. The spherical aberration of the lenses makes it impossible to isolate a single line or even a narrow region; however, the elimination of the energy-rich long wave length part of the spectrum makes it possible to measure the amount of energy absorbed by the acetylene.

The energy measurements were made with a Moll surface thermopile fitted with a fluorite window, and a Leeds and Northrup high-sensitivity low resistance galvanometer. The galvanometer was mounted on a heavy concrete pillar, and deflections of a spot of light were observed on an opaque scale three meters distant from the galvanometer. The system was calibrated by means of a radiation standard lamp furnished by the Bureau of Standards, for which the total radiation in absolute units at two meters' distance in a given direction was known for various values of the current. When the calibrations were made, a shunt was used which reduced the deflections by a factor of 0.336. Following the explicit directions furnished with the lamp, the results summarized in the following table were obtained.

[12] Langer and Meggers, *Bur. Standards, J. Research*, **4**, 711 (1930).

[13] See Hulett, *Phys. Rev.*, **33**, 307 (1911).

[14] Compare Terenin, *Z. Physik*, **31**, 33 (1925); Andrews, *Gen. Electric Rev.*, 817 (1917); and Rubens and Wood, *Phil. Mag.*, **21**, 249 (1911).

TABLE II

CALIBRATION OF THE THERMOPILE AND GALVANOMETER

| Amperes through filament[a] | Ergs / Sq. mm. sec.[b] | Average deflection | Ergs / Sq. mm. sec. per mm. deflection |
|---|---|---|---|
| 0.250 | 4.26 | 24.8 | 0.0172 |
| .300 | 6.27 | 36.25 | .0173 |
| .350 | 8.67 | 49.65 | .0174 |

[a] The current was measured with an accurate ammeter kindly furnished by the Department of Electrical Engineering, University of Minnesota. [b] Calibration of the Bureau of Standards for flux at two meters' distance from the lamp.

The deflections given in column three are the averages of a large number of observations. A series of experiments demonstrated that practically all of the light falling into the thermopile horn is reflected onto the element. The inside diameter of the horn is 2.60 cm.; therefore, the sensitivity may be computed as $0.0173 \times (26.0/2)^2 \times = 9.19$ ergs/sec. per mm. It was determined by experiment that the fluorite window absorbed or reflected approximately 10% of the incident radiation. Applying this correction and the factor for the shunt the final value for the sensitivity is 3.39 ergs/sec. per mm. deflection. While the absorption by fluorite of light of the wave lengths transmitted by the focal isolation device is probably negligible, the reflection amounts to about 8%.[15] It was determined experimentally that the second window of the quartz reaction vessel absorbs and reflects about 20% of the light incident upon it. Therefore, a correction of about 30% must be applied when the intensity of the light passing through the reaction vessel is measured. Applying this correction, the working value of the sensitivity is $3.39 \times 1.30 = 4.40$ ergs/sec. per mm. deflection.

In the final measurements of the quantum yield, a differential manometer was used which was sufficiently sensitive to measure a change in pressure of 0.15 to 0.3 mm. within 2 or 3%. The apparatus consisted of a thin glass diaphragm, the motion of which changed the capacity of a small condenser, which was similar in principle to the device described by Dowling.[16] The modified electrical circuit suggested by Olson and Hirst was used.[17] However, instead of adjusting the resonance circuit until the primary circuit went out of oscillation, it proved more satisfactory to balance the changes in the manometer condenser with the precision variable condenser so as to keep the plate current of the tube in the oscillating circuit constant. Since the highest sensitivity was not necessary in this work, a simplified diaphragm and condenser was used in place of that described by Olson and Hirst. The upper surface of the diaphragm,

[15] "International Critical Tables," Vol. V, p. 257.

[16] Dowling, *Phil. Mag.*, **46**, 81 (1923).

[17] Olson and Hirst, THIS JOURNAL, **51**, 2378 (1930); see also Frank, Thesis, California, **1929**; and Gunn, *Phil. Mag.*, **48**, 224 (1924).

which was a 7.6-cm. No. 00 cover glass sealed to the end of the tube with red sealing wax, was silvered. A mica washer about 0.3 mm. thick (see detail M of Fig. 4) rested on the diaphragm and served to support a 7.6-cm. brass disk. Electrical contact was made with the silvered surface by means of a small piece of platinum foil, which slipped under the mica washer. A few drops of Duco cement served to hold the washer and brass plate in place.

The apparatus was used as a differential manometer. Both sides of the manometer were evacuated simultaneously, and the acetylene was then introduced at the desired pressure. After allowing some time for temperature and pressure equilibrium to be attained, the stopcock (a) was closed.

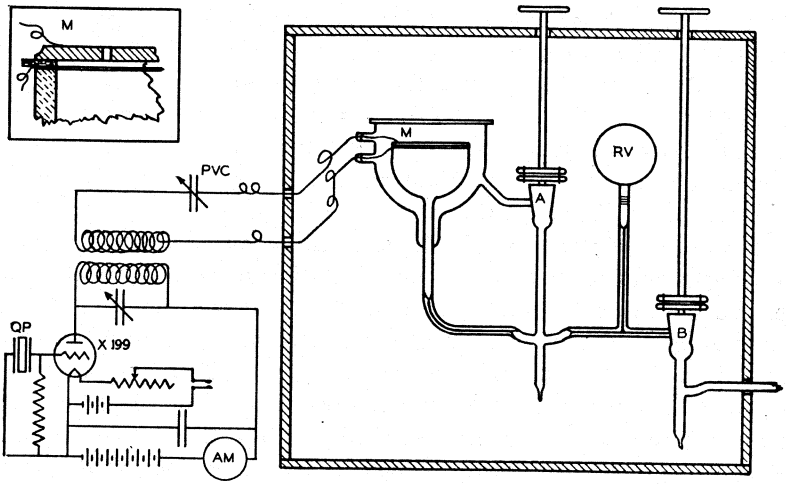


Fig. 4.—The reaction vessel and sensitive manometer.

As is indicated in Fig. 4, the manometer and reaction vessel were both inclosed in an air thermostat, and the stopcock was manipulated by means of a long rod which extended outside of the thermostat. It was found that temperature fluctuations were reduced to a minimum when the thermostat consisted simply of a large box containing a small electric fan. It was necessary to start the fan running at least an hour before beginning an experiment.

The differential manometer was compared to an accurately calibrated McLeod gage, at pressures ranging from 1.5 to 0.2 mm. A plot of the readings of the variable condenser against the differences in pressure gave a smooth curve passing through the origin. Three sets of comparisons were made: one before, one during and one after the quantum yield measurements. All of these results fitted the following semi-empirical equation within 1 or 2%

$$\Delta p = 7.00 \left(\frac{22.12}{C_2}\right)^2 \cdot \frac{\Delta C}{C_1}$$

$$= 3.425 \times 10^4 \cdot \frac{\Delta C}{C_2^2 C_1}$$

where $C_1$ and $C_2$ are, respectively, the initial and final readings of the variable condenser, and $\Delta p$ is the pressure difference in millimeters. The equation corresponds roughly to a sensitivity of about $2.6 \times 10^{-3}$ mm. per division of the condenser scale.

To determine the number of quanta corresponding to the energy absorbed by the acetylene, it is necessary to know the average wave length of the absorbed light. This was determined approximately by comparing a series of spectrograms of the light emerging from the reaction vessel, both when it was evacuated and when it contained acetylene. Since the beam of light was not homogeneous in respect to wave length, and since it could not all be focused on the slit of the spectrograph, a thin ground quartz plate was placed about 5 cm. in front of the slit to scatter the light. A small quartz spectrograph was used, and the spectrograms were taken on oiled process plates, prepared according to the directions of Lyman.[18] The absorption was appreciably only in the region between 2200 and 2050 Å., the lower limit of transmission of the apparatus. The average wave length of the absorbed light was estimated, somewhat arbitrarily, as 2150 Å. This result seems to be in good qualitative agreement with the measurements of Kistiakowsky[19] and of Stark and Lipp[20] on the absorption of ultraviolet light by acetylene. Kistiakowsky[19] found that a very faint series of bands appeared at wave lengths as great as 2400 Å. A more intense series was observed at approximately λ2290 Å. The occurrence of a continuous absorption, possibly due to residual traces of impurities, made it impossible for him to continue his measurements below λ2250 Å. He states, "It is, of course, not excluded that the bands here reported are also to be ascribed to impurities. On the other hand, every precaution exercised in purifying acetylene seemed not to affect them in the least." Stark and Lipp[20] report a series of bands beginning at λ2200 Å. and becoming increasingly intense with decreasing wave length. Herzberg[21] has recently reported that "acetylene has no absorption until λ2070 Å. at pressures up to 30 mm. and 20 cm. length of absorption tube." This statement is not necessarily contradictory to the results presented here, nor to the measurements of Kistiakowsky or of Stark and Lipp, all of which were performed at much higher pressures. As additional evidence that the absorption measurements presented here were not appreciably affected by the presence of impurities, the following results may be cited. In the experiments summarized in Table III the energy absorbed was measured at half-hour intervals during the course of the experiments (from three to four hours). In no case was any systematic trend in the

[18] Lyman, "Spectroscopy in the Extreme Ultraviolet," **1928**, p. 61.

[19] Kistiakowsky, *Phys. Rev.*, **37**, 276 (1931).

[20] Stark and Lipp, *Z. physik. Chem.*, **66**, 36 (1913).

[21] Herzberg, *Trans. Faraday Soc.*, **27**, 379 (1931).

percentage absorption evident, which indicated that the absorption was not due to a trace of a light-sensitive impurity.

**Preliminary Experiments.**—A few attempts were made to measure the quantum yield using the optical system described, and the quartz spiral manometer. The results of these determinations of the quantum yield are summarized in Table III.

TABLE III

QUANTUM YIELD DETERMINATIONS

| $P_0$, mm. | $t$, °C. | $P$, mm. | Time in minutes | Quanta absorbed | Molecules reacted | $M/m$[a] |
|---|---|---|---|---|---|---|
| 587 | 27 | 1.0 | 220 | $2.3 \times 10^{17}$ | $1.3 \times 10^{18}$ | 5.6 |
| 435 | 27 | 1.4 | 180 | $2.4 \times 10^{17}$ | $1.8 \times 10^{18}$ | 7.5 |
| 410 | 22 | 1.2 | 210 | $2.25 \times 10^{17}$ | $1.5 \times 10^{18}$ | 6.7 |

[a] These values of the quantum yield are somewhat smaller than those upon which our earlier (preliminary) average value was based, since in the earlier computations the reflection errors were neglected and the average wave length was taken as 2300 Å.

**Final Series of Measurements.**—The final series of measurements were made with the differential manometer and with the light source which was used in the preliminary measurements. The method of purification and introduction into the reaction system of the acetylene gas has been described. The total pressure of the acetylene was measured with the quartz spiral manometer. In order to reduce the effect of temperature and electrical fluctuations to a minimum, the thermostat fan was started several hours before each experiment and the oscillator was started at least an hour before the zero reading was taken. The acetylene was allowed to remain in the reaction system for about an hour before the manometer stopcock was closed. After each experiment this stopcock was opened in order that the zero point might be checked. In only one case (Experiment 4) did the zero point shift by more than 2 or 3 divisions.

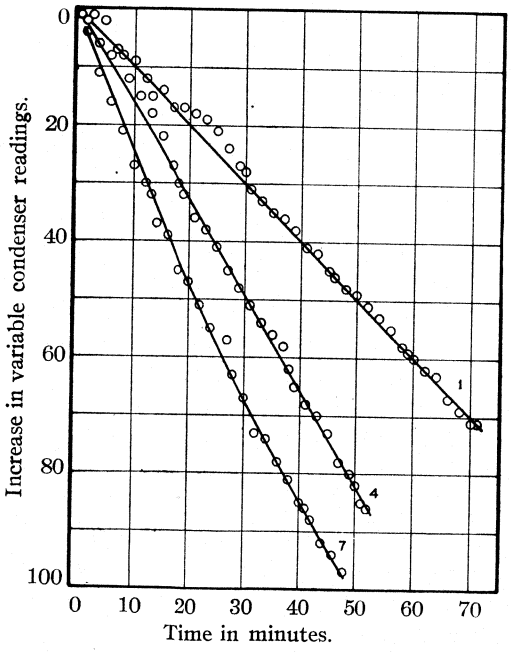


Fig. 5.—Rate of polymerization.

To illustrate the type of pressure variation obtained, the detailed results of several experiments are plotted in Fig. 5. The readings of the

variable condenser are plotted against time in minutes.[22] While the lag which occurred during the first few minutes of each experiment may possibly be due to an induction period, it seems more likely that it is caused by a Draper effect which is not quite sufficient to counterbalance the decrease in pressure due to the reaction.

During each of these experiments, the intensity of the transmitted light was determined at fifteen-minute intervals. The time during which the shutter was down (about ninety seconds for each determination) was subtracted from the reaction time. The percentage of absorption of light by acetylene, for these experimental conditions, was determined in a separate series of experiments. This series of measurements is summarized in Fig. 6. The percentage of the transmitted light absorbed is plotted against the pressure of the gas. Since no difference was observed (in these experiments) when a newly cleaned arc was substituted for a badly discolored one, it is very probable that the brownish film was equally opaque to light of all wave lengths transmitted by the focal isolation device.

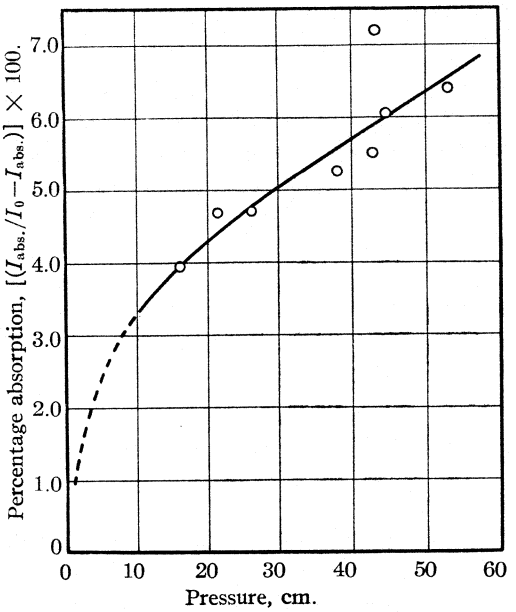


Fig. 6.—Absorption of light by acetylene as a function of pressure.

The results of the seven experiments of this series are summarized in Table IV. The pressures listed in column two are the initial pressures of the acetylene. The total change in pressure in *millimeters* is given in column three and the corresponding decrease in the number of acetylene molecules in column seven. The duration of the experiments, in minutes, is given in column four. The average energy of the absorbed light and the corresponding total number of quanta absorbed are given in columns five and six, respectively. The quantum yield is given in the last column. These experiments were performed at average temperatures between 24 and 25°, with the exception of experiment 3, which was performed at 27°.

It is apparent that, within the limits of experimental error, the quantum

[22] It should be remembered that the intensity of the incident radiation decreased from 10 to 35% during each experiment. The resulting decrease in rate is partly compensated for by the non-linear relation between pressure and condenser readings.

TABLE IV

DETERMINATION OF THE QUANTUM YIELD

| No. | $P$, mm. | Mm. | $t$, minutes | Ergs per second | Quanta absorbed $\times 10^{-16}$ | Molecules reacted $\times 10^{-17}$ | $M/q$ |
|---|---|---|---|---|---|---|---|
| 1 | 217 | 0.218 | 72 | 116 | 5.50 | 5.55 | 10.1 |
| 2 | 235 | .172 | 83 | 116 | 6.33 | 4.30 | 6.8 |
| 3 | 315 | .234 | 54 | 162 | 5.75 | 5.95 | 10.3 |
| 4 | 319 | .341 | 54 | 186 | 6.60 | 8.65 | (13.1) |
| 5 | 365 | .312 | 80 | 151 | 7.95 | 7.65 | 9.6 |
| 6 | 395 | .178 | 56 | 178 | 6.54 | 4.52 | (6.9) |
| 7 | 416 | .253 | 52 | 202 | 6.90 | 6.42 | 9.3 |
| | | | | | | | Av. 9.2±1.0 |

yield is not a function of either the pressure of the acetylene or of the intensity of the absorbed light. In computing the average value of the quantum yield, experiments 4 and 6 have been excluded; experiment 4 because the zero reading of the manometer condenser changed by 10 divisions during the experiment, experiment 6 because the arc was unsteady during the experiment. The average value of the other five experiments is 9.2. This value is probably correct (for the wave length and temperature used) within 10, or at most 15%, uncertainty. It is noteworthy that it is about half the yield per ion pair (9); that is, it is approximately equal to the average yield per ion.

In conclusion we wish to express our gratitude to Dr. Buchta, of the Department of Physics, for his helpful advice and hearty coöperation.

## Summary

1. Acetylene is polymerized to a yellowish solid (resembling cuprene) when it is irradiated by ultraviolet light, in the absence of mercury vapor.

2. Light of λ2537 Å., or longer, is not effective in producing the photochemical polymerization.

3. The rate of polymerization apparently depends only on the intensity of the absorbed light and is otherwise independent of the pressure of the acetylene.

4. It has been shown that the 10° temperature coefficient has a value of 1.25, when acetylene at 10 cm. pressure is exposed to the complete radiation of a quartz mercury arc.

5. The quantum yield of the polymerization, for an average wave length of 2150 Å., is 9.2 ± 1.5. This value appears to be independent of the pressure of the acetylene and of the intensity of the absorbed radiation.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

# THE HEAT CAPACITIES AT LOW TEMPERATURES OF THE SULFIDES OF COPPER AND LEAD[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED AUGUST 4, 1931 PUBLISHED JANUARY 7, 1932

As a part of the general program of the 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 and calculated the entropies of the sulfides of copper and lead. A previous report has been presented on the sulfides of manganese, iron and calcium.[3] As in the case of the latter sulfides, the heat capacities of the oxides of copper and lead had been previously determined.[4]

Since the last report an entirely new wiring system, switchboard and vacuum line have been installed. All wires from the calorimeter to the switchboard, located behind the potentiometer, have been placed in a flexible metal conduit, which has improved the shielding of the electrical circuits and has proved to be a much more satisfactory arrangement than the previous method of stringing single wires. The wires collect no dust nor do they swing in the earth's magnetic field and cause variations in the potentiometer readings. The volt box correction was redetermined after the new wiring was installed by the same method as described previously.[5] The thermocouple was again compared with a standard between sets of measurements and the standard cell checked as usual. Otherwise the method and accuracy are practically the same as have been described previously.

## Materials

The sample of cuprous sulfide was made by the carbon dioxide–carbon disulfide method used for the preparation of the sulfides of manganese, iron and calcium. Analysis of the material after preparation showed it to contain considerable cupric sulfide. To remove this excess sulfur the sample, in a silica flask, was placed in a furnace, evacuated and heated to about 860°. Cupric sulfide is dissociated under these conditions, and excess sulfur distilled off. The resulting sulfide was crystalline, and analyzed 99.8% $Cu_2S$. It had a density of 5.76 at 22.4°. The calorimeter was filled with 315.5 g.

[1] 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] Anderson, THIS JOURNAL, 53, 476 (1931).

[4] Millar, *ibid.*, 51, 215 (1929); Nernst and Schwers, *Sitz. preuss. Akad. Wiss.*, 355 (1914).

[5] Anderson, THIS JOURNAL, 52, 2296 (1930).

The sample of cupric sulfide used was the natural mineral covellite. It was kindly furnished by Mr. R. E. Head, Microscopist of the United States Bureau of Mines at the Intermountain Experiment Station, Salt Lake City, Utah. It had been obtained by him from the Tacoma smelter of the American Smelting and Refining Company. This specimen was very carefully cleaned on an emery wheel. All small spots of silica were removed, as well as any spots which indicated the presence of chalcocite. After cleaning, the sample was crushed and screened. The fines were discarded. The electrolytic deposit from this sample was within 0.02% theoretical for CuS. No measurable impurities could be found. It had a density of 4.64 at 21.2°. A 263.6-g. sample was studied.

Two samples of lead sulfide were studied, (1) a sample of galena which was also obtained through Mr. Head from the Joplin district, and (2) a lead sulfide prepared by the carbon dioxide–carbon disulfide method. The most satisfactory method found for analyzing the lead sulfides was by precipitating the lead as the molybdate. Considerable effort was expended to prepare the sample as pure as possible. After preparation of the sample and repeatedly heating the evacuated sample, the analysis did not improve. On the last heating the furnace was at a higher temperature than previously and permitted the sulfide to distil from the bottom. It condensed in the neck and upper part of the flask. While cooling, the flask cracked, oxidizing a small part of the material. On breaking the flask a grayish powder was found in the bottom. Qualitative tests on this powder showed it to contain iron as well as copper. It was necessary to re-treat the sample with the carbon dioxide–carbon disulfide mixture. After treatment, small portions were placed in a heavy-walled silica tube about 20–25 cm. long, with a constriction about 7–10 cm. from the bottom. A silica tube was attached to the upper part leading through the furnace for evacuating. The galena distilled from the bottom to the upper part, leaving a small amount of residue. The tube was broken after cooling and the distillate removed. The residue in the lower part, as well as the small amount of distillate above the main portion, was discarded. This procedure was repeated several times on the entire sample. The resulting sulfide had a galena structure and the composition PbS, within the accuracy of analysis (0.1%). The calorimeter contained 431.0 g. of the lead sulfide. Its density was found to be 7.57 at 22.4°.

Analysis of the galena indicated that it was pure to within the limits of analytical error (0.1%). The calorimeter was filled with 468.2 g. Its density was also measured at 22.4° and found to be 7.57.

Screen tests using Tyler standard screens were made on these materials and are shown in Table I. Coarser material was used in these measurements than previously. All the samples were −14 mesh.

TABLE I

SCREEN SIZES (TYLER) OF SAMPLES

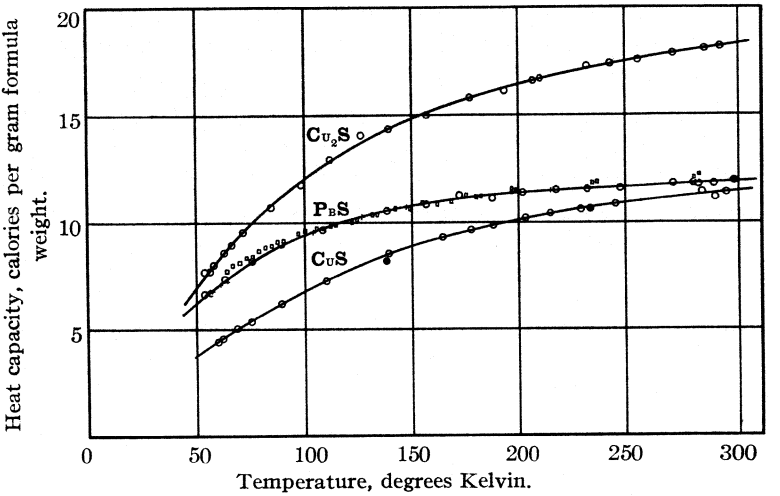
| Screen size | $Cu_2S$, % | Covellite, % | Galena, % | PbS, % |
|---|---|---|---|---|
| +35 | 51.4 | 59.5 | 52.0 | 49.1 |
| +48 | 24.0 | 16.5 | 17.7 | 21.2 |
| +65 | 14.8 | 12.5 | 14.5 | 16.1 |
| +100 | 8.8 | 10.5 | 13.3 | 13.0 |
| −100 | 1.0 | 1.0 | 2.5 | 0.6 |

## The Specific Heats

No previous low temperature measurements have been made on cuprous sulfide. Russell[6] has determined the mean specific heat of cupric sulfide

[6] Russell, *Physik. Z.*, **13**, 59 (1912).

at three points, and Eastman and Rodebush[7] have determined the specific heat of a sample of galena. The results of these investigators, together with those obtained in this Laboratory on the heat capacities of cuprous sulfide, covellite, galena and lead sulfide, expressed in gram calories (15°) per gram formula weight, are shown graphically in Fig. 1. The experimental determinations of the heat capacities are shown in Tables II to V. In converting joules to calories, the factor 1/4.184 was used. The calculations were made on the basis of Cu = 63.57, Pb = 207.20 and S = 32.06.




○, Anderson; +, Anderson, PbS; □, Eastman and Rodebush, galena; ●, Russell, CuS.

Fig. 1.—The heat capacities of cuprous sulfide, covellite, galena and lead sulfide in calories per gram formula weight.

It is to be noted that the determinations on the heat capacity of the prepared lead sulfide coincide with the smooth curve of galena, and also that this curve is below that of Eastman and Rodebush at both the lowest

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CUPROUS SULFIDE

| $T$, °K. | $C_p$ | $T$, °K. | $C_p$ | $T$, °K. | $C_p$ |
|---|---|---|---|---|---|
| 58.0 | 7.988 | 97.6 | 11.71 | 210.4 | 16.68 |
| 53.7 | 7.674 | 111.6 | 12.91 | 232.5 | 17.27 |
| 56.1 | 7.677 | 126.0 | 14.05 | 243.0 | 17.39 |
| 62.6 | 8.567 | 139.0 | 14.33 | 255.6 | 17.56 |
| 66.1 | 8.931 | 157.0 | 14.99 | 271.4 | 17.86 |
| 71.3 | 9.524 | 177.2 | 15.80 | 285.4 | 18.08 |
| 84.4 | 10.68 | 193.3 | 16.13 | 292.2 | 18.18 |
| | | 206.8 | 16.59 | | |

[7] Eastman and Rodebush, THIS JOURNAL, **40**, 489 (1918).

TABLE III

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF COVELLITE (CuS)

| $T$, °K. | $C_p$ | $T$, °K. | $C_p$ | $T$, °K. | $C_p$ |
|---|---|---|---|---|---|
| 59.8 | 4.413 | 139.0 | 8.509 | 229.7 | 10.56 |
| 61.9 | 4.548 | 164.4 | 9.279 | 245.4 | 10.81 |
| 68.6 | 5.041 | 177.6 | 9.618 | 284.1 | 11 37 |
| 75.1 | 5.344 | 188.0 | 9.822 | 289.9 | 11.10 |
| 89.0 | 6.179 | 203.2 | 10.16 | 294.6 | 11.34 |
| 109.9 | 7.241 | 215.4 | 10.39 | | |

TABLE IV

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF GALENA (PbS)

| $T$, °K. | $C_p$ | $T$, °K. | $C_p$ | $T$, °K. | $C_p$ |
|---|---|---|---|---|---|
| 53.7 | 6.626 | 138.2 | 10.51 | 247.5 | 11.55 |
| 56.5 | 6.700 | 156.5 | 10.82 | 271.3 | 11.76 |
| 63.0 | 7.338 | 172.1 | 11.24 | 280.4 | 11.78 |
| 75.6 | 8.167 | 201.9 | 11.36 | 282.6 | 11.74 |
| 89.2 | 8.950 | 218.3 | 11.48 | 289.4 | 11.75 |
| 108.1 | 9.634 | 232.7 | 11.53 | | |

TABLE V

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF LEAD SULFIDE (SYNTHETIC SAMPLE)

| $T$, °K. | $C_p$ | $T$, °K. | $C_p$ | $T$, °K. | $C_p$ |
|---|---|---|---|---|---|
| 54.0 | 6.530 | 76.2 | 8.206 | 215.7 | 11.47 |
| 57.3 | 6.762 | 103.8 | 9.511 | 233.7 | 11.50 |
| 61.1 | 7.078 | 126.4 | 10.24 | 281.7 | 11.87 |
| 64.2 | 7.483 | 147.4 | 10.68 | | |

and highest temperatures. From the galena, lead sulfide results we may assume that the specific heat of natural chalcocite would be the same as that of the prepared sample. Several samples of supposedly pure chalcocite were analyzed, but all were found to contain from 5 to 30% covellite.

**Calculation of Entropies.**—The usual graphical method was employed in calculating the entropies. The experimental heat capacity curves were extended and coincided with Debye functions having the following parameters ($\Theta$): for $Cu_2S$, 92; covellite, 166; and galena and PbS, 107. In Table VI are given the results of the entropy calculations.

TABLE VI

ENTROPY DATA

| | $Cu_2S$ | Covellite | Galena and PbS |
|---|---|---|---|
| Extrap. (0–56.2) °K. | 6.06 | 2.64 | 5.30 |
| Graph. (56.2–298.1) °K. | 22.80 | 13.29 | 16.56 |
| $S°_{298}$ | $28.9 \pm 0.5$ | $15.9 \pm 0.3$ | $21.9 \pm 0.4$ |

Debye and Einstein functions of the following combinations were found to fit the specific heat curves per formula weight of these sulfides.

$$C_{Cu_2S} = D\frac{(92)}{T} + D\frac{(379)}{T}$$

$$C_{CuS} = D\frac{(166)}{T} + E\frac{(428)}{T}$$

$$C_{PbS} = D\frac{(107)}{T} + 2D\frac{(320)}{T}$$

The $Cu_2S$ combination fits the experimental heat capacity curves up to 115°K., that for CuS to 130°K., and PbS to 80°K. By use of the function sums the entropies at 298°K. are 28.8, 15.8 and 21.8 units, respectively, a difference of only 0.1 unit in each from the experimental values.

**Related Thermal Data.**—The heats of formation of cuprous and cupric sulfides have been determined by v. Wartenberg[8] by direct combination of copper with sulfur. For cuprous sulfide he gives −19,000 cal., and for cupric sulfide −11,600 cal. Using the entropy values given above and the values 7.92 for copper and 7.6 for sulfur, the free energy of cuprous and cupric sulfides may be calculated from the thermodynamic equation $\Delta F = \Delta H - T\Delta S$, as −20,640 and −11,720 cal., respectively. Günther[9] has recalculated Thomsen's[10] value for the heat of formation of lead sulfide as −20,900 cal. Berthelot[11] gives −20,300 as the heat of formation. Taking the average value of −20,600 cal. as the heat of formation of lead sulfide, the value of 15.63 as the entropy of lead, 7.6 as that of sulfur and the entropy obtained for lead sulfide, the free energy was calculated as −20,200 cal.

## Summary

The heat capacities of cuprous sulfide, covellite, galena and lead sulfide from about 55 to 300°K. have been determined, and their corresponding entropies and the free energies calculated. The following table contains the summarized results.

| | $S°_{298}$ | $\Delta F°_{298}$ | $\Delta H°_{298}$ |
|---|---|---|---|
| $Cu_2S$ | 28.9 | −20,640 | −19,000 |
| CuS | 15.9 | −11,720 | −11,600 |
| PbS | 21.9 | −20,200 | −20,600 |

BERKELEY, CALIFORNIA

[8] V. Wartenberg, *Z. physik. Chem.*, **67**, 446 (1909).

[9] Günther, *Z. Elektrochem.*, **23**, 197 (1917).

[10] Thomsen, "Thermochemistry," Longmans, Green and Co., London, **1908**, p. 309.

[11] Berthelot, "Thermochemie," Vol. II, **1897**, p. 341.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# THE FREEZING POINTS OF THE TWO FORMS OF METHYLENE IODIDE

BY HOSMER W. STONE

RECEIVED AUGUST 5, 1931 PUBLISHED JANUARY 7, 1932

The freezing point of methylene iodide was determined as the guide to the purity of a sample of the substance which was to be used as a solvent for selenium. The irregularities found, led the writer to investigate this property thoroughly.

The substance exhibits the unusual characteristic of having two transition points between the liquid and the solid state which are less than half a degree apart. A further unusual feature of this compound is that the solid form, which has the lower transition temperature, is the unstable one. Published values of these freezing points for the same form differ by more than a degree centigrade. Experimental work indicated that the most trustworthy value was 0.3° too low.

When liquid methylene iodide is immersed in an air-bath surrounded by ice water the unstable form having the lower freezing point usually separates at a definite temperature. An unstable equilibrium between this form and the liquid has been maintained for several hours despite stirring. It is said to be unstable because sudden cooling of the equilibrium mixture or seeding with the stable form causes the temperature to rise to the freezing point of the more stable form. The stable form may be prepared by immersing the liquid iodide directly in the ice water cooling bath without the intervening air-bath. This causes the material to cool more rapidly and results in the separation of the stable form. These facts agree with what one would expect of a substance showing a monotropic change such as is diagrammed by Ephraim.[1]

Values for the freezing points of these two forms of methylene iodide taken from the literature together with values obtained by the writer are given in Table I.

TABLE I

FREEZING POINTS OF THE TWO FORMS OF METHYLENE IODIDE IN DEGREES CENTIGRADE

| Author | Unstable | Stable |
|---|---|---|
| Beckmann[a] | 4 | 4.47 |
| Bruni and Callegari[b] | 5.23 | 5.7 |
| Tammann and Hollmann[c] | .. | 5.73 |
| This Laboratory | 5.54 | 6.01 |

[a] Beckmann, *Z. physik. Chem.*, **46**, 853 (1903). [b] Bruni and Callegari, *Atti Roy. Acad. Rome*, Series 5, **13**, 481 (1904). [c] Tammann and Hollmann, "Kristallisieren und Schmelzen," Barth, Leipzig, **1903**, p. 278.

[1] Ephraim, "A Text-Book of Inorganic Chemistry," Gurney and Jackson, London, **1926**, p. 49, Figure 19.

**Purification of Methylene Iodide.**—The red color due to iodine, which methylene iodide always develops on exposure to the light, was removed by treatment with sodium thiosulfate which had previously been dried for about twenty hours in an oven at 120°. This decolorized material was shaken and allowed to stand overnight with anhydrous calcium chloride. It was then distilled from a water-bath at about 86° and 30 mm. pressure. These conditions of distillation were not determined accurately but frequent observation during the course of a distillation showed no material change. The samples so prepared were clear and of a light yellow color and remained so while protected from the light. Samples taken at different stages of the distillation showed excellent agreement in freezing points.

It was found that when a single sample was used repeatedly for freezing point determinations, there was a gradual lowering of the freezing point to a limit of about 0.05°. Two samples which approached this limit became cloudy on cooling as though an emulsion were being formed. It was found that by shaking a 25-cc. sample with an excess of water (one drop gave an excess) both the approximate lowering of 0.05° and the emulsion like cloudiness could be duplicated. Because of these facts the observations reported were made on freshly distilled samples and these used for but one set of determinations.

**Calibration of Thermometers.**—The Fahrenheit thermometer (Bureau of Standards No. 32818) was certified in February, 1924, to have a correction of minus 0.10° when the reading was 32.00° and a correction of minus 0.22° when the reading was 60.00°. An ice-point determination agreed exactly with this calibration. Interpolation gave a correction of minus 0.14° to be applied to the observed freezing points of the unstable modification of methylene iodide and a correction of minus 0.15° to be applied to the observations of the freezing point of the stable modification.

The Centigrade thermometer bore the Bureau of Standards No. 39197. The certificate was dated July 8, 1926. A zero ice-point correction and one of 0.07° at a reading of 10.00° was certified. An ice-point determination indicated an error of minus 0.06° which, together with the minus 0.04° obtained from the interpolation of the Bureau of Standards figures, gave a total correction of minus 0.10° to be applied to the observed readings over the range of both the unstable and the stable forms of methylene iodide.

**Method of Freezing Point Determination.**—The methylene iodide in a glass tube surrounded by an air-bath was immersed in an ice-water bath. A stopper supporting the thermometer and a glass stirring rod was placed in the tube containing the methylene iodide so that the thread of the mercury was completely immersed when the readings were taken. These were taken through the air-bath and ice water with a thermometer magnifier. Work was carried out in a partly darkened room so that the samples showed no color change such as accompanies exposure to light.

TABLE II

FREEZING POINTS OF METHYLENE IODIDE

| Sample number | Unstable form: Corrected value | Unstable form: Convert. to °C. | Stable form: Corrected value | Stable form: Convert. to °C. |
|---|---|---|---|---|
| Thermometer Number 32818 | | | | |
| 103 | 41.96 | 5.533 | 42.77 | 5.983 |
| 106[a] | 41.99 | 5.544 | 42.87 | 6.040 |
| 107[a] | 41.95 | 5.527 | 42.80 | 6.000 |
| 107[b] | 41.98 | 5.545 | 42.82 | 6.011 |
| Average | | 5.537 | | 6.008 |
| Thermometer Number 39197 | | | | |
| 101 | | 5.54 | | 5.98 |
| 102 | | 5.54 | | 6.02 |
| 104 | | 5.52 | | 6.01 |
| 105[a] | | ... | | 6.02 |
| 105[b] | | 5.52 | | 5.99 |
| 107[c] | | 5.55 | | 6.02 |
| Average | | 5.534 | | 6.007 |

Eight determinations with a Beckmann thermometer of the difference in the freezing points of the two forms varying between 0.468 and 0.477 gave an average value of 0.473°. The close agreement of this with the difference obtained by the less precise calibrated thermometers is further evidence for the trustworthiness of the determinations. It may also be noted that this difference agrees with that given by the other workers quoted in Table I.

## Conclusions

A method of obtaining the two forms of methylene iodide is given.

The unique relations between the two forms with respect to transition points and stability have been confirmed. It appears to be a monotropic dimorphous substance.

The close accord in the values obtained by the use of two independent standards is such as to establish the values for the freezing points of the two forms of methylene iodide as 5.54 and 6.01°, respectively. These values are probably correct within 0.02°.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

# THE CATHODE RAY TUBE IN THE X-RAY SPECTROSCOPIC ANALYSIS OF COLUMBIUM AND TANTALUM

BY GORTON R. FONDA

RECEIVED AUGUST 6, 1931 PUBLISHED JANUARY 7, 1932

A method of analysis using cathode rays was recently developed and applied with success to the analysis of several series of binary alloys.[1] In this method the sample to be analyzed is placed in the open air above the window of a Coolidge cathode ray tube and is excited directly by the electron beam.

This method has now been applied to the analysis of tantalum and columbium mixtures. A Seemann spectroscope was used and a current of hydrogen was passed through it to decrease the absorption of the radiation of longer wave length. The Hevesy method was followed of calibrating against a comparison element. For the analysis of columbium a sodium chloride crystal was used and the K radiation studied. For tantalum the choice was made of the L radiation and in order to record its longer wave length, a crystal was used of beta alumina. This was given us by the Norton Company through the courtesy of Mr. Raymond R. Ridgeway. We are particularly indebted to him for it, since it proved to be very much better than any samples of gypsum available. The lattice spacing on the cleavage face was determined to be 11.00 Å.

The cathode ray tube was operated as before in a vertical position from a regulated DC circuit with a current of 0.2 ma. at 86.0 kv. A jet of hydrogen was played between the window of the tube and the sample. It gave such effective cooling that no change could be observed in the physical condition of the sample nor was there any noticeable evaporation. Repetitions of an exposure upon the same sample gave always the same relative intensities of its constituents.

**Factors Affecting Intensity.**—It is desirable to discuss some general features of the procedure, particularly to bring out the various factors which influence the intensity of the radiation. Exposures involving comparison were made on pieces of film cut from the same strip and their development was carried out together in the same bath.

The position of the sample was important. The window itself had a diameter of 7 mm. In the present experiments the intensity of radiation was increased by placing the edge of the sample 1 mm. from the edge of the window, and by increasing the angle between specimen and window from 10 to 20°, beyond which there was no further advantage.

The radiated spot in the specimen showed a uniform luminescence, as estimated visually, over an area having a width in the horizontal plane of 9 mm. This distribution of electron energy is a distinct advantage, for it checks the heating of the sample. It leads to no loss in efficiency when the Seemann spectroscope is used.

[1] G. R. Fonda and G. B. Collins, THIS JOURNAL, **53**, 113 (1931).

In this instrument a wedge of tungsten is placed directly above the crystal, so that the distance between them constitutes the slit width. The wedge, crystal and photographic film are part of a fixed system which is rocked as a whole rather than simply the crystal alone. The intensity of the recorded line is not inversely proportional to the rocking angle, as is the case with collimating slits, but depends upon the width of the irradiated area and its intensity distribution. This was demonstrated by recording the intensity of the $K\alpha$ doublet of molybdenum for several angles, setting the spectroscope each time so that the swing took place with a symmetrical distribution on each side of the critical angle between the crystal and the central point of the irradiated area.

| Rocking angle..... | 1° | 2° | 3° | 4° | 6° |
|---|---|---|---|---|---|
| Intensity..... | 1.00 | 0.88 | 0.71 | 0.49 | 0.28 |

Another factor is the position of the tube. When the intensity from molybdenum was measured with the cathode ray tube in a horizontal position and the molybdenum plate in a vertical position, the irradiated area thereby became such that its maximum dimension lay in a vertical position. Its width was reduced to about 2.5 mm. and this proved to be so important that the intensity fell to 50%. The vertical position of the tube was therefore chosen for all other experiments.

In order to have the maximum intensity available, the slit width was maintained at 0.50 mm. This was insufficient to resolve the $K\alpha$ or $L\alpha$ doublets, but there seemed to be no disadvantage in basing a quantitative determination upon the peak of their combined intensity. To reduce the absorption a slow current of hydrogen was passed through the spectroscope. A measure of the improvement is shown in Table I from measurements made on the relative absorption of the $K\alpha$ doublets of iron and titanium.

TABLE I

RELATIVE ABSORPTION OF AIR AND HYDROGEN

| Element | Wave length, $K\alpha_1$ | Absorption, % In air | Absorption, % In $H_2$ | Absorption coef. of $H_2$ |
|---|---|---|---|---|
| Fe | 1.93 | 63 | 4 | 0.0010 |
| Ti | 2.74 | 94 | 63 | .025 |

The wave lengths under investigation in the analytical work were all of them below the $K\alpha$ line of iron and therefore in a range in which absorption was negligible in the presence of hydrogen.

There is another variable factor of influence upon the intensity ($I$) of radiation from the target and that is the voltage ($V$) of the electrons in terms of the excitation voltage ($V_0$). For both $K$ and $L$ radiation the relationship holds $I = k(V - V_0)^x$. For the lower voltage ranges there is general agreement that $x$ approximates 2. In the case of aluminum targets upon which the electron beam impinges normally and from which the x-radiation is observed at an acute angle, Lorenz[2] has observed that at higher voltage ratios of $V/V_0$, the intensity increases less markedly and finally decreases when the ratio exceeds about 10. The explanation lies in the greater penetration of electrons which occurs as their voltage is increased. As a result proportionately more x-radiation is generated at such greater depths that more material is interposed to its emission and its absorption becomes greater.

Fonda and Collins have shown that, under excitation by a cathode ray tube, the exponent remained 2 up at least to voltage ratios of 4 for molybdenum and 11 for iron, with no indication of a change in slope. These measurements have now been repeated photographically with the same results. Additional measurements have been made with elements whose radiation is of still longer wave length. For the $K\alpha$ doublet of titanium

[2] Lorenz, *Z. Physik*, **51**, 71 (1928).

at 2.743 Å., a value for the exponent of about 1.4 was found for the range in voltage ratio of 8–16. The result remained the same whether the specimen was placed at a 45 or 10° angle and whether a crystal of gypsum or of beta alumina was used. For the K$\alpha$ doublet of calcium at 3.352 Å. about the same slope was obtained at a 10° angle over a range of 9–16. From that point up to a value of 20 the increase in intensity was very much less. This is evidently the same phenomenon which Lorenz observed with aluminum radiation of 8.319 Å. at as low a voltage ratio as 10.

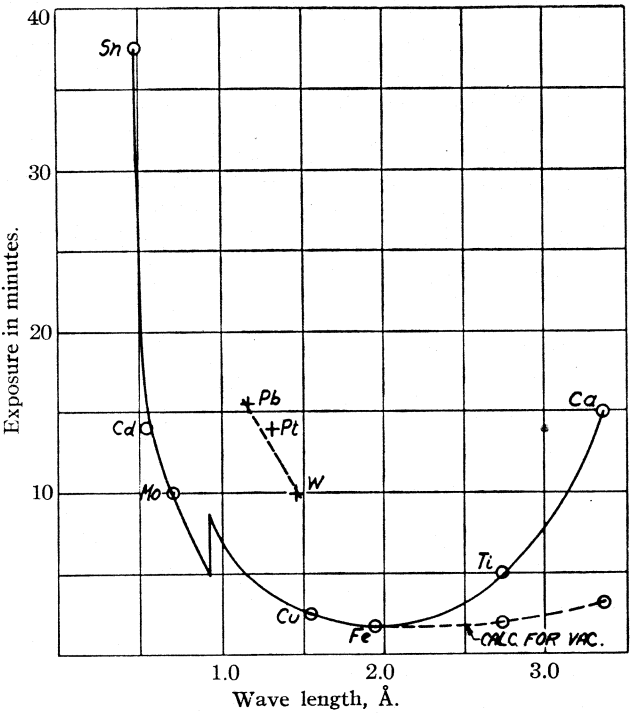



Fig. 1.—Time of exposure required for constant density of $\alpha$ doublet: ——K radiation, – – – –L radiation.

The indication is therefore that the eventual decrease in intensity occurs at a voltage ratio which becomes greater as the atomic number of the element involved becomes higher. This is a reasonable consequence of the increase in penetrating power of characteristic radiation which develops as the element emitting it becomes of higher atomic number.

For the L radiation of a tungsten target, placed at a 20° angle to the aluminum window, it was found that the exponent remained definitely 2 over the range in voltage ratio of 4 to 9.

It is helpful to know the variations in time of exposure in hydrogen that are required for the various elements involved. Measurements were made with polished metallic plates and the results for both the K$\alpha$ and L$\alpha$ doublets are shown graphically in Fig. 1 in terms of the time needed to produce the same photographic density of line. The time for columbium is about the same as for molybdenum, and that for tantalum the same as for tungsten, as each of these pairs is of adjoining elements.

The decrease in time of exposure observed up to 2 Å. is due both to the continuous decrease in excitation voltage and to the increasing photographic activity of the film. Beyond iron the absorption even in hydrogen becomes appreciable, and the time of exposure increases.

The dotted curve gives the results as calculated for vacuum. The slight increase for longer wave lengths is undoubtedly due to the diminished effect of high voltages in increasing the intensity of the characteristic radiation from elements of such low atomic number.

The time required to give a moderately strong density for the copper K$\alpha$ doublet at 86.0 kv. and 0.2 ma. was two and one-half minutes. This is to be compared with the time of one minute cited by Hevesy, Böhm and Faessler[3] for exciting the copper K$\alpha_1$, $\alpha_2$ lines by secondary radiation at 50 kv. and 20 ma.

A peculiar phenomenon was encountered when the intensity of radiation from a polished plate was compared with that from powder of the same metal. In the cases of the K$\alpha$ doublet from molybdenum at 0.708 Å., from copper at 1.537 Å. and from iron at 1.932 Å., no difference whatever resulted, despite the wide range of wave length involved. With L radiation, however, the intensity of the $\alpha$ doublet from the powder was found to be only 66% that from the plate for the cases of lead at 1.172 Å., and of tungsten at 1.518 Å. The behavior of tungsten trioxide was more nearly normal, for with a target made of it the intensity was 85% that from the polished metal plate.

**Calibration for Columbium.**—It was aimed to have present in a mixture sufficient of a comparison element so that a characteristic line in its spectrum might have the same density as one of the elements under analysis. The molybdenum K$\alpha$ doublet was chosen as the basis of comparison. As molybdenum is of adjacent atomic number to columbium, there were no complicating features. The combined effect of several characteristic factors was to increase the relative intensity of the columbium by about 2%.

The columbium oxide used was a Fansteel product and was found spectroscopically to be free of tantalum to less than 2%. This was mixed with metallic molybdenum powder. For equality of density of both lines the relation was found to hold that 1 g. of molybdenum is equivalent to 0.949 g. of columbium. With molybdenum oxide as the source of the comparison element, about the same factor resulted. The crystal of alumina gave the same relationship of intensities in both the first and second order as the crystal of sodium chloride, but the latter was used in all quantitative work. The relationship remained the same on adding an amount of FeO equal to that of the $Cb_2O_5$ and also an amount of $WO_3$ equal to four times the weight of the $Cb_2O_5$. Zirconium, which in appreciable amounts would have had an effect, was rarely encountered, and then in amounts no larger than 1%.

Comparison was also made with columbium carbide. The factor obtained was 0.936, virtually the same as with the oxide. This result is in accord with those experiments in which the intensity of K radiation was found to be the same, independent of the physical condition of the metal.

**Calibration for Tantalum.**—The $Ta_2O_5$ used for calibration was a

[3] Hevesy, Böhm and Faessler, *Z. Physik*, **63**, 74 (1930).

Fansteel product and was found to be free of columbium to less than 0.1%.

The crystal of beta alumina required for the relatively long wave length involved had the curious characteristic of recording a shadow on the short wave length side of the line, a phenomenon undoubtedly due to excessive penetration of the crystal by x-radiation with corresponding reflection from layers of atoms at abnormal depths. This prevented the use of tungsten as a comparison element. The second order $K\alpha$ doublet of molybdenum was sufficiently remote to be free of this difficulty. The density of the general radiation serving as a background to the two lines was found to be constant, within the limits of measurement, over the range covered by them. Equal density of line resulted from a mixture containing 1 g. of molybdenum to 0.656 g. of tantalum.

The $K\alpha_1$ line of molybdenum at 0.708 Å. is so remote from the absorption edge at 1.252 Å. of the tantalum $L_I$ radiation that excitation should be negligible. This was demonstrated by finding that the relative densities of the two lines remained unaffected (1) on adding an amount of $Cb_2O_5$ equal to 1.12 the weight of $Ta_2O_5$; and (2) on diluting the mixture with alumina equal in weight to 60% of the $Ta_2O_5$ content.

Tantalum is generally accompanied in its ores by iron. In the presence of sufficient iron the tantalum $L\alpha$ line at 1.518 Å. is reduced in intensity as the result of absorption of its radiation by iron, the absorption edge of whose K radiation is at 1.740 Å. The calibration of $Ta_2O_5$ with molybdenum in the presence of FeO is given in Table II and is shown graphically in Fig. 2. There is given also the relationship for equality of the $K\alpha$ doublet of iron and the second order $K\alpha$ doublet of molybdenum, to be used as a guide in estimating the amount of iron present.

TABLE II

RELATIONSHIP FOR EQUAL DENSITY OF LINE IN $Ta_2O_5$–FeO MIXTURES

| $Ta_2O_5$, % | FeO, % | G. of Ta equivalent to 1 g. of Mo | G. of Fe equivalent to 1 g. of Mo |
|---|---|---|---|
| 48.7 | 51.3 | .. | 0.235 |
| 48.9 | 51.1 | 0.790 | .. |
| 62.1 | 37.9 | .705 | .246 |
| 77.0 | 23.0 | .674 | .270 |
| 100.0 | 0 | .656 | .. |

This relationship can hold only for fairly high concentrations of $Ta_2O_5$ and FeO, as was demonstrated by diluting the mixture containing 62.1% $Ta_2O_5$ and 37.9% FeO with an amount of alumina equal to five times the weight of the $Ta_2O_5$, so that the percentages were reduced to 20.7% $Ta_2O_5$ and 12.6% FeO. A test upon it showed that equal density of line resulted for the proportion of 1 g. of molybdenum to 0.649 g. of $Ta_2O_5$, about the same value found in the absence of iron.

A similar calibration was carried out between molybdenum and tungsten, the element adjoining tantalum. Equal density of line resulted for the mixture containing 1 g. of molybdenum to 0.655 g. of tungsten. For the same atomic percentage this is equivalent to 0.647 g. of tantalum, about the same as found directly. This is a desirable confirmation of the calibration for tantalum, for no complete analysis of the $Ta_2O_5$ had been made. Very pure tungsten oxide is obtainable and the close agreement would indicate that the $Ta_2O_5$ also is of a high purity.

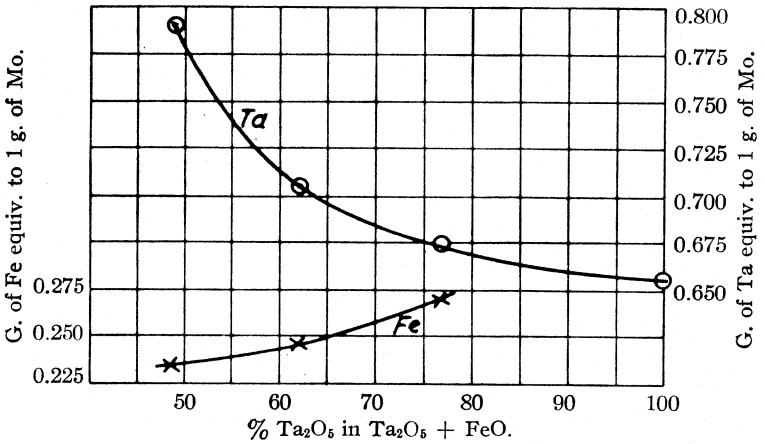



Fig. 2.—Effect of iron upon calibration for tantalum.

It has already been noted that the intensity of the L$\alpha$ doublet of tungsten is lower for metal powder than for oxide powder. This indicates that the intensity from a metal depends upon the element with which it is combined in a compound. A calibration carried out with the carbide showed that its L radiation is less than that observed from the oxide. The extent of the reduction is the same for tungsten as for tantalum. Table III shows the relationship in terms of molybdenum as the comparison element. It is noteworthy that the intensity of radiation from tantalum becomes less as the density of packing of the metallic atoms becomes greater and also as the angle of the sample is decreased. The intensity of the K$\alpha$ doublet of molybdenum remained the same at both angles.

TABLE III

DEPENDENCE OF CALIBRATION UPON NATURE OF COMPOUND

| Metal | Angle of sample | G. of metal equivalent to 1 g. of Mo | | |
|---|---|---|---|---|
| | | Element | Carbide | Oxide |
| Tungsten | 20° | 1.17 | 0.946 | 0.655 |
| Tantalum | 20° | .. | .938 | .655 |
| Tantalum | 45° | .. | .73 | .50 |

These observations are so unusual that further experiments were made to test their validity, choosing for study the difference between the intensity

of the $L\alpha$ doublet from tungsten as metal and as oxide. This difference was found to persist (1) when the source of the oxide was oxidized metal; (2) when dry mixtures were rubbed on filter paper without the use of paste; (3) when the oxide was tested in a jet of air instead of hydrogen; (4) when the metal was mixed with 16% boric acid by weight (71% by volume) to reduce its density; (5) when $MoO_3$ or $Ta_2O_5$ was used as the source of the comparison element, instead of metallic molybdenum; (6) when the voltage was reduced from an electron velocity of 80.4 kv. to one of 39.5 kv. In all of these cases the relative intensities of the $\alpha_1$ and $\beta_1$ lines remained unaltered. It would seem then that the differences observed for tungsten and tantalum in the intensity of their L radiation as dependent upon the character of the compound represent an inherent feature of their radiation and are not due to accidental causes. The matter is being pursued further.

## Results

This spectroscopic method has been used in the analysis of ores and oxides, both in their original state as well as in products obtained during their purification and separation. In practice analyses have been made on amounts of $Ta_2O_5$ from 0.8 to 89% and on $Cb_2O_5$ from 0.1 to 26%. The time of exposure depends upon the amount of the element present. For the proportions mentioned it has varied from twenty minutes to three hours.

The error in analysis is probably about 2%. This is an absolute error so that the greater value attaches to the determination of small amounts. In three cases the mixtures of oxides examined were free from foreign material. Their analysis is therefore of interest because the sum of the $Ta_2O_5$ and $Cb_2O_5$ found indicates directly the accuracy attainable. Separate determinations were of course made for each. The results are given in Table IV. In the case of one mixture, an opportunity was presented to compare the results of the spectroscopic examination with those obtained by a chemical analysis carried out through the courtesy of Professor H. C. Fogg of the University of New Hampshire, using the Marignac method[4] with modifications introduced by himself. Through him and Professor Daggett of the same institution, an analysis was made of mixture No. 3. The results are in surprisingly good agreement.

TABLE IV

ANALYSIS OF PURE OXIDE MIXTURES

| Method of anal. | Sample | $Ta_2O_5$, % | $Cb_2O_5$, % | Total, % |
|---|---|---|---|---|
| Spectroscopic | No. 1 | 80.7 | 21.2 | 101.9 |
| Spectroscopic | No. 1 | 80.7 | 21.0 | 101.7 |
| Spectroscopic | No. 2 | 75.0 | 24.0 | 99.0 |
| Spectroscopic | No. 3 | 77.0 | 19.5 | 96.5 |
| Chemical | No. 3 | 76.5 | 19.3 | 95.8 |

[4] Marignac, *Ann. Chim. Phys.*, **8**, 60 (1866).

Mixture No. 1 was the result of a chemical separation from an ore of the combined oxides of tantalum and columbium. It was carried out through the kindness of J. H. Christopher of this Laboratory. The yield amounted to 62.5% so that the analysis of the oxides corresponds to a content in the ore of 50.5% $Ta_2O_5$ and 13.2% $Cb_2O_5$. Direct analysis of the ore yielded the values of 50.3% $Ta_2O_5$ and 12.2% $Cb_2O_5$. Such good agreement is of importance. It demonstrates that the intensity of the tantalum and columbium lines, as registered in oxides, is not disturbed when the metals are present in a tantalite as acid salts. This is in agreement with the conclusion of Hevesy and Böhm,[5] who failed likewise to find any difference in calibration as dependent on the occurrence of tantalum in the oxide or in the ore.

Before closing the author would like to express his appreciation of stimulating conversations with Dr. W. P. Jesse.

## Summary

1. Further experiments have been made with the Coolidge cathode ray tube as a means of exciting x-radiation.

2. The variation of intensity of spectral lines has been studied as related to operating conditions and to the element examined.

3. Calibration and analyses have been carried out for tantalum and columbium in tantalites and mixtures of oxides and carbides. Molybdenum was used as a comparison element.

4. For the limited number of elements examined, differences in intensity of the L$\alpha$ doublet were found to exist depending upon the nature of the chemical compound and upon the angle of the specimen. No similar differences were found in the intensity of the K$\alpha$ doublet.

SCHENECTADY, NEW YORK

[5] Hevesy and Böhm, *Z. anorg. Chem.*, **164**, 69 (1927).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

# THE PHOTOCHEMICAL POLYMERIZATION OF CYANOGEN

BY T. R. HOGNESS AND LIU-SHENG TS'AI

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Cyanogen, when heated, forms a solid polymerization product known as paracyanogen, having the empirical formula $(CN)_x$. Its structural formula is unknown, but by analogy with the polymerization products of cyanogen halides[1] it has been assumed that three molecules of cyanogen form one molecule of paracyanogen. Polymerization has been effected not only by heating[2] but by photochemical means and by bombardment with $\alpha$-particles[3] as well. Berthelot and Gaudechon[4] carried out the photochemical polymerization in a very qualitative way, and their results gave only the information that the reaction was a photochemical one and that it could be effected by light of convenient frequency. In beginning the more detailed study of this reaction, we found that we were quite unable to reproduce their work, and that the problem was somewhat more difficult of attainment than their results seemed to indicate.

## Absorption Measurements

Before beginning the photochemical investigation, it was necessary to obtain information regarding the absorption spectrum of cyanogen. To this end we first employed a Hilger E-2 quartz spectrograph, a hydrogen discharge tube, and a quartz absorption cell 20 cm. long filled with cyanogen at one atmosphere. With the dispersion afforded by this spectrograph we obtained a set of diffuse bands to the short wave length side of about 2230 Å. To determine whether these bands were really diffuse or whether they appeared so through lack of dispersion of our instrument, we made new photographs employing the larger Hilger E-1. This instrument gives a dispersion of approximately 1.5 Å. per mm. in the neighborhood of 2200Å. Even with this dispersion, which should certainly resolve any bands due to as light a molecule as cyanogen, the bands still appeared diffuse. Using the lines of the copper arc as standards of comparison, the wave lengths of the bands were measured. Table I gives the limits of each of these bands.

The lowest wave length observed corresponds to the limit of transmission of the quartz. It will be observed that there is no regularity in either the width of each band or in their relative positions.

The fact that the absorption bands are diffuse has led us to the conclusion

[1] Mulder, *Rec. trav. chim.*, **5**, 84 (1886); **6**, 199 (1887).

[2] Troost and Hautefeuille, *Compt. rend.*, **66**, 795 (1868).

[3] Lind, Bardwell and Perry, THIS JOURNAL, **48**, 1556, 1575 (1926).

[4] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

TABLE I

WAVE LENGTH LIMITS OF THE ABSORPTION BANDS OF CYANOGEN IN ÅNGSTRÖM UNITS

| | | |
|---|---|---|
| 2240–2241 | 2203–2202 | 2171–2168 |
| 2230–2227 | 2196–2190 | 2162–2157 |
| 2219–2216 | 2186–2176 | 2152–2149 |
| 2207–2206.5 | 2175–2173 | 2146–2145 |
| 2205–2204 | | |

that the primary step in the process is one of predissociation; that the $C_2N_2$ molecule upon light absorption dissociates. Cyanogen may dissociate on light absorption either into two cyanogen radicals (one may be in the excited state) or into $N_2$ and $C_2$. From our usual conception of the structure of the cyanogen molecule, one would presuppose that the former products rather than $N_2$ and $C_2$ would be formed. This is substantiated by the fact that in our later photochemical experiments no evidence of free carbon was found and by the fact that Berthelot and Gaudechon[4] found neither nitrogen nor carbon as a polymerization product. Furthermore, on passing a weak discharge through cyanogen, only the CN bands were observed.

All the evidence points to the dissociation of cyanogen into CN radicals. The following simple thermochemical calculation will show that such a dissociation is possible

| | |
|---|---|
| $C_2N_2 + 2O_2 = 2CO_2 + N_2$ | $\Delta H = -260$ k. cal.[5] |
| $2CO_2 = 2C(S) - 2O_2$ | $\Delta H = +188$ k. cal.[6] |
| $2C(s) = 2C(v)$ | $\Delta H = +300$ k. cal.[7] |
| $N_2 = 2N$ | $\Delta H = +207$ k. cal.[8] |
| $2C(v) + 2N = 2CN$ | $\Delta H = -376$ k. cal.[9] |
| $CN = CN^*(^2\Sigma)$ | $\Delta H = +41$ k. cal.[9] |
| $C_2N_2 = CN + CN^*(^2\Sigma)$ | $\Delta H = +100$ k. cal. |

The energy corresponding to the band of the longest wave length observed is 127 k. cal., sufficient to give the products indicated above. A similar calculation shows that this limiting wave length is sufficient to dissociate the cyanogen molecule into normal $N_2$ and $C_2$, but not if one of these products is to be in any one of the known excited electronic states.

Our calculation has shown that the absorbed energy is sufficient to dissociate the $C_2N_2$ molecule into a normal CN radical and a CN radical either in the $^2\Sigma$ state (3.19 volts) or in the $^2\pi$ state (1.78 volts). The CN radicals in either of these states should give rise to fluorescent radiation if the pressure were such that little damping of that fluorescence took place. Inasmuch as cyanogen absorbs light only very weakly at low pressure, it

[5] "International Critical Tables," Vol. V, p. 167.

[6] *Ibid.*, Vol. V, p. 181.

[7] Kohn and Guckel, *Naturwiss.*, **12**, 139 (1924).

[8] Mullikan and Birge, *Nature*, **122**, 844 (1928).

[9] Villars, THIS JOURNAL, **52**, 61 (1930).

would hardly be expected that such a fluorescence could be detected and, in fact, all efforts to obtain any trace of fluorescence were in vain. We employed as a light source a zinc spark, a cadmium spark and a hydrogen discharge tube and in all cases the pressure of the absorbing gas was in the neighborhood of 1 mm. This pressure we guessed to be about an optimum one in view of the small absorption of this gas, and the maximum damping pressure of others. Using the Steinheil spectrograph ($f = 2.8$), with several exposures of six to twelve hours each we obtained no trace of a fluorescence spectrum.

The fact that no fluorescence was obtained does not argue against the assumption that one of the CN radicals is left in an excited state. Were the absorption as great as that of iodine, one might use such an argument, but in this case the absorption is considerably less.

The wave length of the effective light was such that in our photochemical experiments we were unable to use a monochromator but the range was so narrow (2240–2145 Å.) that this was unnecessary. We could without any appreciable error assume a mean effective wave length of 2150 Å. We did not therefore determine wave lengths but rather determined the total absorption in the same cell that was used in the photochemical experiments.

The variations in intensity of the light source used in the absorption measurements (described later) and the unsteadiness of the thermopile circuit were large enough so that we could not with assurance use the usual method of measuring the light intensity with a full and empty cell alternated in the light path. We found that the following method gave reproducible results.

The absorption cell was a cylindrical tube 25 mm. long and 2 cm. in diameter with quartz windows at each end. This tube was connected with an intervening stopcock to a liter bulb which in turn was connected to a mercury reservoir. Acting similarly to a Töpler pump, the gas in the one-liter bulb could be compressed into the absorption cell and the stopcock closed. The one-liter bulb could be evacuated by lowering the mercury reservoir and then upon opening the stopcock the gas could be expanded to about 125 times its initial volume and the pressure reduced correspondingly.

The procedure then was to have the light from the hydrogen discharge tube pass through the absorption cell full of gas and onto the thermopile. When the galvanometer in the thermopile circuit was exceptionally steady, the stopcock was opened, the gas in the cell expanded, and the deflection of the galvanometer noted. In all the absorption measurements the gas was at a pressure of one atmosphere in the absorption cell. When the stopcock was opened, the gas remaining was at a pressure of about 6 mm., and this latter pressure we considered to be ineffective in our calculations.

The result of ten individual experiments gave an absorption of 8.8 ($\pm 0.6$) % of the total radiation passing through the cell.

### Determination of Quantum Efficiency

Preliminary experiments with the quartz mercury vapor lamp, the cadmium spark, the zinc spark and the hydrogen discharge tube as light sources showed that only the latter could be used effectively in this experiment.

Berthelot and Gaudechon obtained an 18.5% contraction in volume when cyanogen was subjected to the radiation of a quartz mercury vapor lamp. Repeating this work and loading our lamp to its full capacity, we were unable to obtain any appreciable volume contraction in this time. A consideration of the emission spectrum of the mercury lamp and the absorption spectrum of cyanogen makes it improbable that such an effect should be observed when pure cyanogen was used, since there are no emission lines in the region of absorption. The same is true for the cadmium spark. The spectrum of the zinc spark shows strong lines below the limit of absorption, but these were apparently not of sufficient intensity after passing through the quartz window, or they occurred in a region of no absorption. Lacking details we cannot venture any explanation of Berthelot and Gaudechon's positive results other than that their cyanogen contained some sensitizing agent.

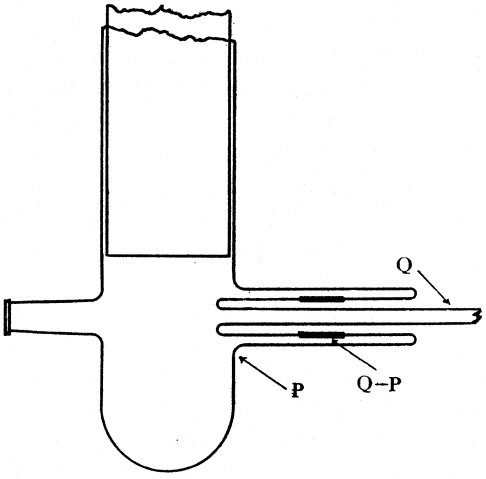


Fig. 1.—P, Pyrex; Q, quartz; Q—P quartz–Pyrex seal.

The hydrogen discharge tube was a modification of the one described by Lawrence and Edlefsen.[10] Instead of using sealing wax to join the quartz tube to the Pyrex electrode cylinders, we used a quartz–Pyrex seal as shown in Fig. 1. The current was supplied through a 6600 volt 25 k. v. a. transformer equipped with a resistance in the primary circuit. The usual operating voltage and current through the tube were 3000 volts and 5 to 6 amperes, respectively. With this load the tube usually broke down at the end of about two weeks of running.

The cyanogen used in all these experiments was prepared by heating recrystallized silver cyanide in a previously evacuated line. Before being used the gas was dried over phosphorus pentoxide and purified by three fractionations.

The decrease in the amount of cyanogen in any single run was so small

[10] Lawrence and Edlefsen, *Rev. Sci. Instr.*, **1**, 45 (1930).

that we were unable to employ the usual manometric method with mercury as the manometer medium. We had to resort, therefore, to the use of some organic liquid as the manometer medium, employ a tilted mercury manometer, or use a horizontal tube containing a bead of mercury. The last two methods have the disadvantage that the mercury tends to stick to the sides of the tube but since cyanogen is slightly soluble in organic liquids and since the rate of pressure decrease was so small, we adopted the last-named method, *i. e.*, the horizontal tube holding a bead of mercury. When precautions were taken to have the capillary tube very clean and the mercury very pure, and with continual tapping of the tube, consistent results were obtained. The apparatus used to determine the rate of volume decrease was nothing more than the cell used in the absorption measurements connected to the capillary as a side tube. This tube was placed in the path of the light beam near the discharge tube and the thermopile immediately behind it. The cell was shielded and its temperature at all times known by means of Beckmann thermometers.

As the reaction proceeded, the polymer formed as a faint cloud and settled to the bottom of the tube. Unfortunately some of the polymer gathered on the end windows and only the first part of each run could be used for our calculation. Knowing the rate of volume decrease and the light intensity, and after integrating the intensity over the cross section of the light beam and calibrating the thermopile against a standard lamp, we were able to calculate the quantum efficiency. Table II gives the results of six runs.

TABLE II

QUANTUM EFFICIENCY OF POLYMERIZATION OF CYANOGEN

| Run | Length of run, min. | No. of molecules of $(CN)_2$ polymerized | No. of quanta absorbed | Moles per einstein |
|---|---|---|---|---|
| 1 | 21 | $5.8 \times 10^{17}$ | $2.22 \times 10^{17}$ | 2.6 |
| 2 | 25 | $10.1 \times 10^{17}$ | $3.28 \times 10^{17}$ | 3.1 |
| 3 | 18 | $6.4 \times 10^{17}$ | $2.74 \times 10^{17}$ | 2.4 |
| 4 | 22 | $8.9 \times 10^{17}$ | $3.02 \times 10^{17}$ | 3.0 |
| 5 | 24 | $10.6 \times 10^{17}$ | $2.68 \times 10^{17}$ | 3.0 |
| 6 | 25 | $9.7 \times 10^{17}$ | $2.9 \times 10^{17}$ | 3.3 |
| | | | Av. | 3.0[a] |

[a] One run gave a value of 4.6 moles per einstein for the quantum efficiency. Since this value deviated from the mean to a much larger extent than the others (over 50%) we have felt justified in omitting this from the table.

In the calculation we have used 2150 Å. as the mean wave length. This mean was selected by an examination of the photograph of the absorption spectrum.

The paracyanogen was distinctly brown in color. Upon heating it *in vacuo* the product volatilized, leaving no solid residue.

Since there was some mercury vapor present in our cell, the question might naturally arise as to the possibility of photochemical sensitization by the mercury. To test this we made a run with the mouth of a small flask of boiling mercury just under the path of the beam between the discharge tube and the absorption cell. There was no apparent difference between the polymerization rates with and without the intervening mercury vapor. The reaction in our case, therefore, was not due in any appreciable extent to a sensitized reaction.

## Discussion

The low quantum efficiency obtained for this reaction precludes any long chain reaction accounting for the mechanism of polymerization. As the first step of the mechanism we feel that the evidence given by the diffuse bands and the lack of free carbon points to a dissociation into CN radicals.

$$(CN)_2 + h\nu = 2CN, \text{ or}$$
$$(CN)_2 + h\nu = CN + CN'$$

The simplest mechanism to account for a quantum efficiency of three moles per einstein would have as the second step

$$CN + C_2N_2 \longrightarrow (CN)_3$$

The last product could, if unstable, then form a larger group by secondary polymerization.

Although we have obtained only diffuse bands in the absorption spectrum, Henri[11] in a table in his "Structure des Molecules" gives a region of fine structured bands from 2385 to 2200 Å. With a tube 20 cm. long filled with cyanogen to one atmosphere pressure we did not detect the faintest trace of these bands. We can only surmise that Henri's cyanogen contained some foreign matter. The same, we suspect, applies to the work of Berthelot and Gaudechon, since cyanogen does not absorb any of the lines of the quartz mercury vapor lamp.

Lind, Bardwell and Perry[3] in their work on the polymerization of cyanogen by $\alpha$-particles found that about seven molecules polymerized per ion pair. The mechanisms in their case and that in ours are apparently different. There is no reason to suppose that these mechanisms should be the same in the two cases, particularly since no long chain reaction is involved. These authors described their product as a black polymer. The product in our case was distinctly brown. This difference, however, might easily be accounted for by the small side reaction liberating nitrogen, which these authors found.

## Summary

1. The absorption spectrum of cyanogen consists of a series of diffuse bands extending from 2240 Å. to the limit of transmissivity of quartz.

[11] V. Henri, "Structure des Molecules," J. Hermann et Cie, Paris, France, p. 99.

2. The conclusion is drawn that upon absorption of light between 2145 and 2240 Å., cyanogen dissociates (predissociation) into either two normal CN radicals or one normal and one excited.

3. No cyanogen fluorescence was obtained.

4. The quantitative absorption of light by cyanogen in the region 2145 to 2140 Å. was determined.

5. The quantum efficiency for the photochemical reaction $(CN)_2 \longrightarrow$ paracyanogen was determined to be three moles per einstein.

6. A brief discussion of the mechanism, together with a discussion of the results of other investigators on the polymerization of cyanogen, concludes the work.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# THE DENSITY AND SURFACE TENSION OF LIQUID HYDROGEN FLUORIDE

BY J. H. SIMONS AND J. W. BOUKNIGHT

RECEIVED AUGUST 8, 1931 PUBLISHED JANUARY 7, 1932

Hydrogen fluoride is a substance of considerable interest because of its unusual properties.[1] The vapor has been shown to consist of an equilibrium between HF and $H_6F_6$.[2] There are, however, very few available data about the anhydrous liquid upon which one may even make assumptions as to the molecular condition in the liquid state. This is of particular interest because the heat of vaporization as calculated from the vapor pressure curve[3] is constant over a wide temperature range. The heat of vaporization calculated in this manner is for one mole of the gas independent of the weight of the molecules. As the apparent molecular weight of the gas changes considerably with temperature and the heat of polymerization[2] is fairly high, one may be led to assume that the liquid has the same apparent molecular weight as the gas. Kolosovskii[4] has assumed this at the boiling point, because the liquid obeys Trouton's rule. This would seem to be a peculiar behavior. The material presented in this paper represents the beginning of an attack upon this problem.

The anhydrous liquid was prepared in the manner described by Simons[3] and was condensed directly into the apparatus in which it was to be used.

**The Density.**—The apparatus used to make the density determinations is shown in Fig. 1. This consisted of a cylindrical vessel of copper 2.5 cm.

[1] For a review of this subject see "Hydrogen Fluoride and Its Solutions," Simons, *Chem. Reviews*, **8**, 213 (1931).

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

[3] Simons, *ibid.*, **46**, 2179 (1924). In this paper an error is made in calculating $\Delta H$, which should be 6025 calories per mole.

[4] Kolosovskii, *Bull. soc. chim.*, **41**, 422 (1927).

in diameter and 20 cm. long. Six copper trays which fitted into the upper part of the cylinder were provided on which to place chemicals to prevent hydrogen fluoride vapor from escaping or water from entering. All joints were made with silver solder. A copper bob which was immersed in the liquid was suspended from the arm of a balance by a number 40 copper wire. This wire extended through the 2-mm. holes provided in the trays and their cover. The lower three trays were filled with pulverized sodium fluoride and the upper three with pulverized anhydrous calcium chloride.

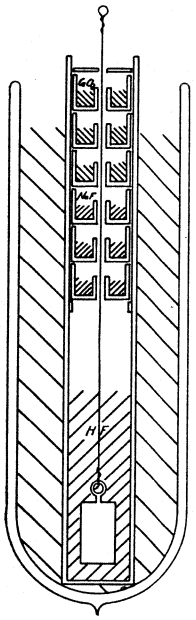

Fig. 1.—Density apparatus for hydrogen fluoride.

The liquid hydrogen fluoride was condensed into the cylinder from the generator using an ice–salt cooling bath. The bob was placed in it, and then the trays containing the chemicals were carefully slid into place with the wire from the bob extending through them. The apparatus was then placed in a Dewar vessel containing solid carbon dioxide and either acetone or ether. The Dewar was placed in a balance, and the bob suspended from the beam. The bob was repeatedly weighed in this manner as the temperature slowly rose. The temperature was determined by means of a calibrated toluene thermometer. A calibrated set of weights was used, and the frost collecting on the wire was carefully removed before each determination. Free swinging of the balance indicated when the wire was not in contact with the walls of the trays. The weight of the bob in air and immersed in water enabled the calculations to be made in the usual manner. Corrections were made for the thermal expansion of copper.

The results are given in Table I and represented graphically in Fig. 2. Gore[5] gives three values (0.9885 at 13.6°, 0.9875 at 12.8° and 0.9922 at 11.1°) which do not lie on the curve, but Hill and Sirkar[6] report a value (1.0005 at 0°) with which we

TABLE I

THE DENSITY OF LIQUID HYDROGEN FLUORIDE

| Temperature, °C. | Density, g./cc. | Temperature, °C. | Density, g./cc. |
|---|---|---|---|
| −73.9 | 1.1828 | −72.9 | 1.1828 |
| −72.9 | 1.1828 | −71.0 | 1.1792 |
| −71.5 | 1.1773 | −67.0 | 1.1708 |
| −68.0 | 1.1705 | −63.0 | 1.1617 |
| −66.0 | 1.1659 | −55.1 | 1.1364 |
| −52.1 | 1.1299 | −49.1 | 1.1222 |

[5] Gore, *J. Chem. Soc.*, **22**, 368 (1869).

[6] Hill and Sirkar, *Proc. Roy. Soc.* (London), **A83**, 130 (1909).

TABLE I (*Concluded*)

| Temperature, °C. | Density, g./cc. | Temperature, °C. | Density, g./cc. |
|---|---|---|---|
| −40.2 | 1.1000 | −46.1 | 1.1121 |
| −35.2 | 1.0831 | −42.2 | 1.1022 |
| −23.8 | 1.0519 | −37.2 | 1.0979 |
| −20.3 | 1.0493 | −33.2 | 1.0827 |
| −16.4 | 1.0389 | −29.8 | 1.0731 |
| −12.4 | 1.0316 | −25.8 | 1.0616 |
| − 7.4 | 1.0199 | −17.8 | 1.0440 |
| | | −13.4 | 1.0354 |
| | | − 9.4 | 1.0252 |
| | | − 5.4 | 1.0136 |
| | | − 1.4 | 1.0047 |
| | | + 4.2 | 0.9918 |

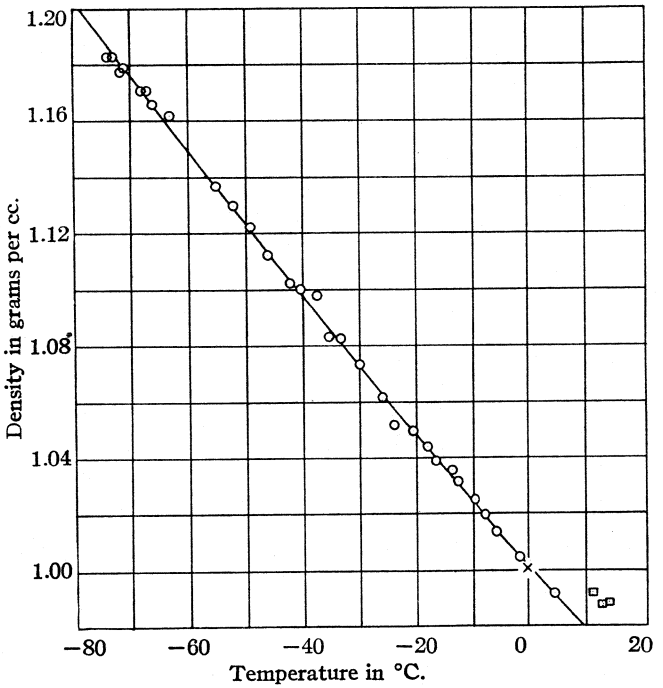


Fig. 2.—The density of liquid hydrogen fluoride. The curve is drawn from the equation given in the text: the circles represent the experimentally determined values, the squares represent the values reported by Gore, and the cross represents the value reported by Hill and Sirkar.

are in very good agreement. The values of Gore can be accounted for by assuming that his liquid contained 1% water. The equation for the curve which falls through the points is

$$d = 1.0020 - 0.0022625t + 0.000003125t^2$$

in which $d$ is the density in grams per cubic centimeter and $t$ is the temperature in degrees centigrade. The probable error is estimated at $\pm$ 0.1% and the maximum error at $\pm$0.2%.

The complete density curve for hydrogen fluoride–water mixtures is given by Hill and Sirkar.[6] From their work it is seen that the determination of density is an excellent method for estimating the amount of water in almost anhydrous hydrogen fluoride. The density changes more than 16% for the first 9% of water.

**The Surface Tension.**—The maximum bubble pressure method of determining surface tension was chosen, because it enabled the determinations to be made by making measurements on an inert gas and avoided the necessity of either seeing the corrosive liquid or making measurements directly upon it.

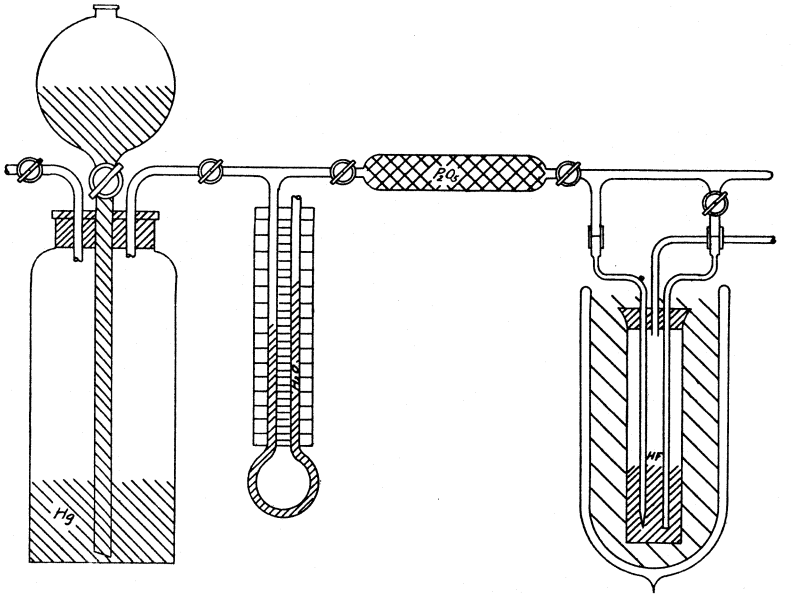


Fig. 3.—Surface tension apparatus for hydrogen fluoride.

A diagram of the apparatus is shown in Fig. 3. Nitrogen from a cylinder was stored in the aspirator using mercury as the impelling liquid. A water manometer was used, and a phosphorus pentoxide tube was located between the manometer and the bubbler to prevent water from reaching the hydrogen fluoride. The bubbler was made entirely of pure silver. A bottle containing a mixture of sodium fluoride and anhydrous calcium chloride into which the exit from the bubbler extended prevented the escape of hydrogen fluoride or the entrance of water. The apparatus was

calibrated with both water and benzene over a range of temperature. The equation given by Sugden[7] was used

$$\gamma = AP\left(1 + 0.69\, r_2 g \frac{D}{P}\right)$$

in which $\gamma$ is the surface tension in dynes per square centimeter, $A$ is a constant for the apparatus, $P$ is the difference in pressure needed to form bubbles from the small tube and the large tube, in dynes per square centimeter, $r_2$ is the radius of the large tube in centimeters, $g$ is the acceleration due to gravity, and $D$ is the density of the liquid in grams per cubic centimeter.

The hydrogen fluoride was condensed into the bubbler, the amount being determined by weighing before and after the condensation. The bubbler was then connected to the rest of the apparatus and immersed in a Dewar vessel containing solid carbon dioxide and acetone. A calibrated toluene thermometer was fitted to the bubbler by means of a copper sheath. The measurements were made as the temperature was allowed to rise slowly. Several check series of determinations were taken.

The results are given in Table II and shown graphically in Fig. 4. The equation for the curve which fits the points is given in the usual form

$$\gamma = 40.7\left(1 - \frac{T}{503.2}\right)^{1.78}$$

where 503.2 is the critical temperature on the absolute scale as determined by Bond and Williams.[8] $T$ is absolute temperature. The estimated error is $\pm 1\%$.

TABLE II

THE SURFACE TENSION OF HYDROGEN FLUORIDE

| Temperature, °C. | Surface tension, dynes/sq. cm. | Temperature, °C. | Surface tension, dynes/sq. cm. |
|---|---|---|---|
| −81.8 | 17.70 | −81.8 | 17.60 |
| −72.4 | 16.20 | −71.9 | 16.48 |
| −64.0 | 15.33 | −65.0 | 15.95 |
| −57.0 | 14.77 | −61.0 | 15.48 |
| −46.1 | 14.10 | −51.4 | 14.30 |
| −43.7 | 13.80 | −44.6 | 14.00 |
| −43.2 | 13.95 | −35.2 | 13.25 |
| −23.2 | 12.00 | −24.8 | 11.93 |
| −16.3 | 11.40 | −16.3 | 11.19 |
| − 7.4 | 10.83 | − 2.4 | 10.43 |
| + 3.6 | 9.85 | + 4.6 | 10.19 |
| +11.3 | 9.68 | +16.0 | 8.87 |
| +16.0 | 9.10 | +18.5 | 8.81 |
| +18.2 | 8.63 | +19.2 | 8.92 |

[7] Sugden, *J. Chem. Soc.*, **125**, 29 (1924).

[8] Bond and Williams, THIS JOURNAL, **53**, 34 (1931).

## Discussion

The surface tension is unusually low. As the Eötvös equation has no theoretical foundation and as hydrogen fluoride is known to have a high dielectric constant and to form conducting solutions, we would not be justified in calculating the molecular weight by this means. However, assuming $H_6F_6$ as the formula for the liquid, the Eötvös constant is 1.52, which is what one might expect for this liquid. Assuming HF, the constant is 0.46, which is much too low a value. Assuming the Eötvös constant 2.0, the molecular weight becomes 180. There is no apparent change of Eötvös constant with temperature. The application of the Eötvös equation indicates that the liquid is polymerized probably to form $H_6F_6$.

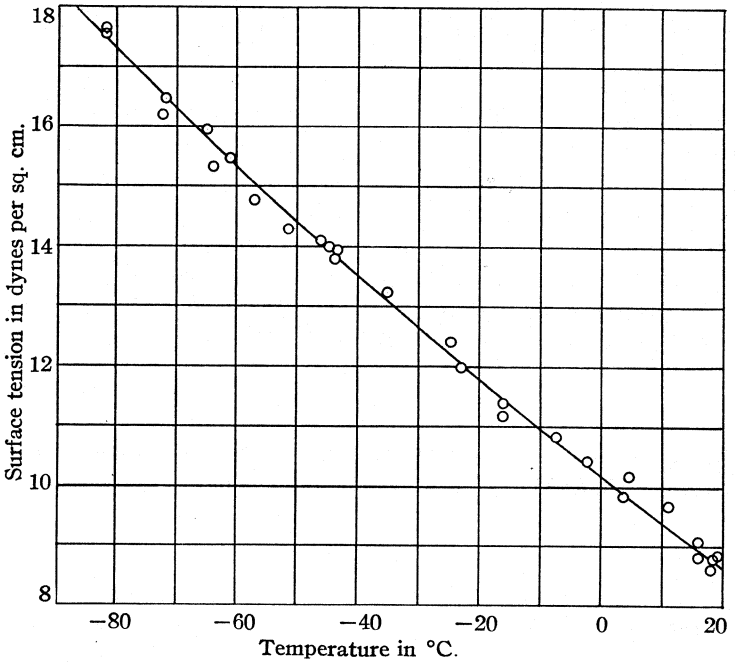


Fig. 4.—The surface tension of hydrogen fluoride. The curve is drawn from the equation given in the text, and the circles represent the experimentally determined values.

A comparison of the surface properties of the hydrogen halides is given in Table III. The densities, surface tension, and $(M/D)^{2/3}\gamma$ are compared at the boiling points, this temperature being chosen as it will approximate a corresponding temperature for the different substances. Although the surface tension and total surface energy increase with formula weight in this series there is much greater difference between HF and HCl than there

is between HCl and HBr or HBr and HI. For the Eötvös constant and $(M/D)^{2/3}\gamma$, $H_6F_6$ seems to fit into the series better than HF.

TABLE III

COMPARISON OF PROPERTIES OF HYDROGEN HALIDES

| Compound | Density at boiling point g./cc. | Surface tension at boiling point, dynes/cm. | $(M/D)^{2/3}\gamma$ at boiling point | Eötvös constant | Total surface energy, $\gamma - T(\partial\gamma/\partial T)$ |
|---|---|---|---|---|---|
| HF | 0.9593 | 8.65 | 65.5 | 0.46 | 35 |
| $H_6F_6$ | | | 216 | 1.5 | |
| HCl | 1.1957 | 23.15 | 226 | 1.5 | 61 |
| HBr | 2.152 | 24.9 | 299 | 2.0 | 70 |
| HI | 2.796 | 26.8 | 344 | 2.0 | 72 |

Different conclusions are arrived at as to the nature of liquid hydrogen fluoride by applying different criteria. Its high dielectric constant and ability to form conducting solutions indicate that it is a polar liquid. Trouton's rule gives a constant 20.6 when calculated in the usual manner and 27 when Hildebrand's modification is used. This fact indicates that the liquid is normal. The value of the Eötvös constant indicates that the liquid is associated; but as it is constant over a wide temperature range, we have a deviation from the usual behavior of associated liquids. This fact may mean that the liquid consists of a single definite polymer. This conclusion is at variance with the conclusion that the liquid has the same molecular species in the same equilibrium as the gas at the same temperature, which might be drawn from the fact that the heat of vaporization per mole is constant over the same temperature range that the Eötvös constant is constant.

## Summary

The density of liquid hydrogen fluoride has been determined from $-75$ to $+5°$. The values fit the equation

$$d = 1.0020 - 0.0022625t + 0.000003125t^2$$

The surface tension of liquid hydrogen fluoride has been determined from $-80°$ to $+19°$. The values fit the equation $\gamma = 40.7\,[1 - (T/503.2)]^{1.78}$.

The surface tension and its temperature coefficient indicate that liquid hydrogen fluoride is probably polymerized.

The nature of liquid hydrogen fluoride as indicated by various criteria is discussed.

EVANSTON, ILLINOIS

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

# THE NORMAL VIBRATIONS OF ACETYLENE

BY A. R. OLSON AND H. A. KRAMERS

RECEIVED AUGUST 11, 1931 PUBLISHED JANUARY 7, 1932

About a year ago Mecke[1] published an analysis of the normal vibrations of acetylene, and used the results to interpret the infra-red spectrum of acetylene which had previously been studied by Levin and Meyer.[2]

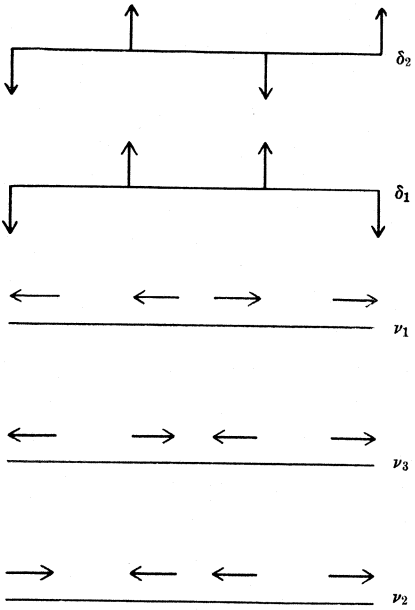


Fig. 1.

In this analysis Mecke assumed a linear model, and listed the five normal modes of vibration shown in Fig. 1. He observed that $\delta_1$ was symmetrical and that $\delta_2$ was antisymmetrical with respect to reflection on the center of gravity, but nevertheless concluded that both were optically active. The ratio of $\delta_1:\delta_2$ which he derived was 1:1.88, and so on this basis he assigned the band at 730 cm.$^{-1}$ to $\delta_1$ and the band at 1326 cm.$^{-1}$ to $\delta_2$.

It seems to the authors of this article that since $\delta_1$ is symmetrical, it cannot be observed in the absorption spectrum except in combination bands, and that the ratio $\delta_1:\delta_2$ must be in error. We have therefore recalculated the frequency ratios for the normal vibrations by classical mechanics. We assume a linear molecule and infinitely small vibrations. The forces are assumed to be such that we can write the potential energy in the first approximation in the form

$$\tfrac{1}{2} K_1 [(\Delta S_1)^2 + (\Delta S_3)^2] + \tfrac{1}{2} K_2 (\Delta S_2)^2 + \tfrac{1}{2} K_3 [(\Delta\alpha_1)^2 + (\Delta\alpha_2)^2]$$

where $K_1$, $K_2$ and $K_3$ are coefficients of the restoring forces, $S_1$, $S_2$ and $S_3$ are equilibrium distances, and $\alpha_1$ and $\alpha_2$ are angles as shown in Fig. 2.

In Fig. 3, which refers to the vibration $\delta_1$, $d$ is the distance between carbon and hydrogen, and $2\,l$ is the distance between the carbons; $\alpha$ is the angle between the C–C bond and the C–H bond. In order that the molecule as a whole shall have no rotation it is necessary that $m_2\, l\dot{x}_2 = (l + d)\, m_1\, \dot{x}_1$ where $m$ is the mass; the subscript 2 refers to the carbon and the subscript 1 to the hydrogen. For small angles we can set $\alpha = \sin\alpha$, and so

[1] R. Mecke, *Z. Physik*, **64**, 173 (1930).

[2] Aaron Levin and Charles F. Meyer, *J. Opt. Soc. Am.*, **16**, 137 (1928).

$\dot{\alpha}d = \dot{x}_1 + j\dot{x}_2$ where $j = (l + d)/l$. The kinetic energy $T = m_1 x_1^2 + m_2\dot{x}_2^2$. By solving for $\dot{x}_1$ and $\dot{x}_2$ in terms of $\dot{\alpha}$, $d$ and $m$ and substituting we get $T = \dot{\alpha}^2 d^2 m_1 m_2/(m_2 + m_1 j^2)$.

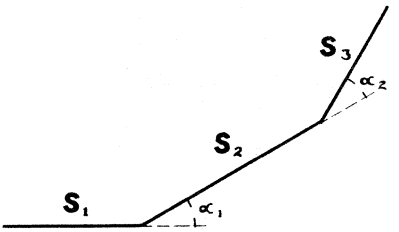

Fig. 2.

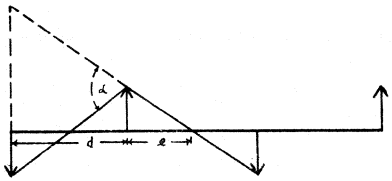

Fig. 3.

In Fig. 4 $\beta$ replaces $\alpha$ as the angle between the two bond directions; otherwise the notation is the same as before. Here we must impose the condition for no translation of the molecule, and so $m_1\dot{x}_1 = m_2\dot{x}_2$.

$\dot{\beta}d = \dot{x}_1 + \dot{x}_2$ and $T$ is again equal to $m_1\dot{x}_1^2 + m_2\dot{x}_2^2$. On substitution we get $T = \dot{\beta}^2 d^2 m_1 m_2/(m_1 + m_2)$. Therefore $\delta_2/\delta_1 = (m_1 + m_2)^{\frac{1}{2}}/(m_1 j^2 + m_2)^{\frac{1}{2}}$.

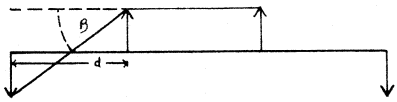

Fig. 4.

We can get a fair estimate of $j$ from Birge's[3] compilation of band spectra data. Setting $2\,l = 1.31$ Å. and $d = 1.13$ Å., we find $j^2 = 7.45$, and so $\delta_2/\delta_1 = 0.816$, compared to Mecke's value of 1.88.

With respect to $\nu_1$, $\nu_2$ and $\nu_3$ we can set up the expressions for the kinetic and potential energies immediately, and from them derive the relation which must hold between these frequencies. The kinetic energy $T$ for all three vibrations will have the form $T = m_1\dot{x}_1^2 + m_2\dot{x}_2^2$ where $x_1$ is the displacement of the hydrogen atom, and $x_2$ is that of the carbon atom.

If $K_1$ is the coefficient of the restoring force between carbon and hydrogen along the bond and $K_2/2$ that between the carbons, then for the vibration $\nu_2$, the potential energy will be given by $V = K_1(x_1 + x_2)^2$ and from the condition for no translation we get $m_1 x_1 = m_2 x_2$.

For the vibrations $\nu_1$ and $\nu_3$ the potential energy takes the form

$$V = K_1 x_1^2 - 2K_1 x_1 x_2 + (K_1 + K_2) x_2^2$$

where $x_1$ and $x_2$ are independent. Solving the equation for the fundamental frequencies by the usual method for small vibrations, we obtain

$$\nu_1^2 : \nu_2^2 : \nu_3^2 = \frac{13\,K_1 + K_2 - (169\,K_1^2 - 22\,K_1K_2 + K_2^2)^{\frac{1}{2}}}{24} : \frac{13\,K_1}{12} : \frac{13\,K_1 + K_2 + (169\,K_1^2 - 22\,K_1K_2 + K_2^2)^{\frac{1}{2}}}{24}$$

These values of $\nu_1$, $\nu_2$ and $\nu_3$ are not inconsistent with Mecke's interpretation

[3] R. T. Birge, "International Critical Tables," McGraw-Hill Book Co., New York, Vol. V, p. 409.

of the spectrum, but if our values of $\delta_1$ and $\delta_2$ are correct some revision of Mecke's correlation with experiments must be made.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# THE TRANSFERENCE NUMBER OF LITHIUM CHLORIDE AS A FUNCTION OF THE CONCENTRATION

BY GRINNELL JONES AND BENJAMIN C. BRADSHAW

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## Introduction

According to the classical dissociation theory of Arrhenius the mobilities of the ions are expected to be independent of the concentration and hence transference numbers should be constants which do not vary with the concentration. On the other hand, according to the modern interionic attraction theory of Debye and Hückel, the mobilities of the ions vary with the concentration and this variation is not relatively the same for all ions but depends on the size of the ions and especially on the valence. Therefore it may be predicted from this theory that transference numbers will vary with the concentration. It has been shown by Jones and Dole[1] that the transference numbers of the barium ion in barium chloride can be expressed by an equation having the form, $t = [A/(1 + B\sqrt{c})] - 1$, (1) over the entire range from 0.001 to 1.0 molal. It was also shown that although erroneous values for the transference number of barium chloride were obtained by Lucasse[2] from data on the electromotive force of concentration cells with and without transference, the fault lay, not in the data themselves, but in their interpretation, and that a more rigid mathematical procedure gave results in essential agreement with the analytical method.

It seemed to be desirable to test the general validity of the equation, $t = [A/(1 + B\sqrt{c})] - 1$, for the variation of the transference number with the concentration. The experimental determination of transference numbers is tedious and difficult and the classical theory gave no incentive for studying the variation of transference numbers with the concentration. These considerations are probably responsible for the fact that sets of data on transference numbers for any salt of sufficient precision for our purpose and covering a wide range of concentration and obtained by the same method are extremely rare in the chemical literature. The most important exception to this general rule is the set of values for lithium chloride from 0.001 to 3.0 normal obtained by the electromotive force

[1] Grinnell Jones and Malcolm Dole, THIS JOURNAL, **51**, 1073 (1929); Malcom Dole, *J. Phys. Chem.*, **35**, 3647 (1931).

[2] W. W. Lucasse, *ibid.*, **47**, 743 (1925).

method by MacInnes and Beattie.[3] These results are shown by the points inside triangles in Fig. 1. It should be noted that the curve depicting these data shows a steep slope at low concentrations.

The equation, $t = [A/(1 + B\sqrt{c})] - 1$, may be readily transformed into $\frac{1}{t+1} = \frac{1}{A} + \frac{B\sqrt{c}}{A}$, (2) and hence if the equation is valid for any values of $A$ and $B$, a straight line should be obtained when $1/(t + 1)$ is plotted against $\sqrt{c}$.

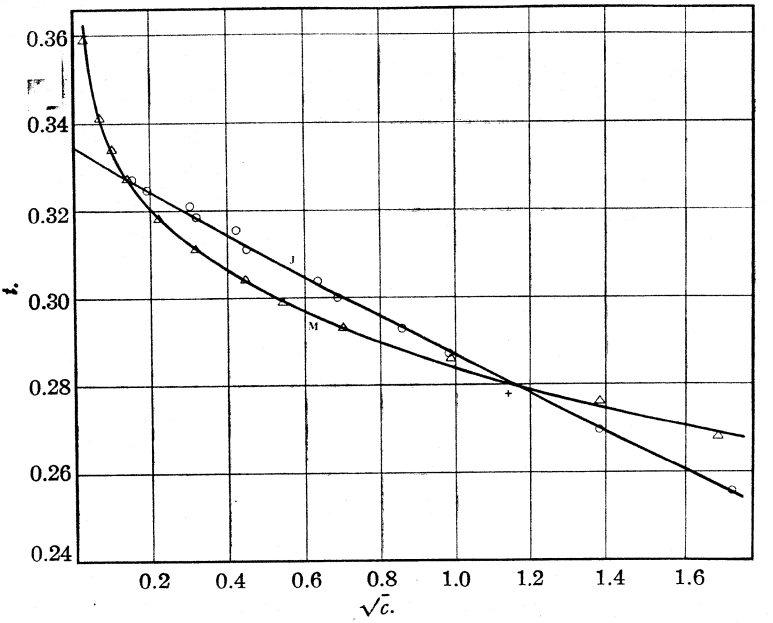


Fig. 1.—Transference number of the lithium ion in lithium chloride, $t$, plotted against $\sqrt{c}$: △, Curve M, MacInnes and Beattie; ⊙, Curve J, Jones and Bradshaw; +, Washburn.

But the values of MacInnes and Beattie do not yield a straight line when plotted in this way (see Fig. 2, points shown inside triangles). This demonstrates that it is impossible to find values of $A$ and $B$ which will make this equation agree with the results of MacInnes and Beattie; but this is not necessarily conclusive against the general validity of the equation because the method of computing the transference numbers used by MacInnes and Beattie was the prototype followed by Lucasse, which has been shown to give erroneous results in the case of barium chloride.

Washburn[4] has determined the transference number of the lithium ion in lithium chloride of 1.25 normal to be 0.279, using the analytical method.

[3] D. A. MacInnes and J. A. Beattie, THIS JOURNAL, 42, 1117 (1920).

[4] E. W. Washburn, *ibid.*, 31, 322 (1909).

This result is shown by a cross in Figs. 1 and 2. Determinations have also been made by Kuschel, by Bein, by Jahn and by Pearce and Mortimer,[5] but the results when plotted are quite erratic.[6]

As a first step in testing the general validity of the Jones and Dole equation we decided to redetermine the transference numbers of lithium chloride over a wide range of concentration by the analytical method. Another object of this investigation was to determine whether or not the electromotive force method when interpreted in the manner developed by Jones and Dole would give the same results as the analytical method.

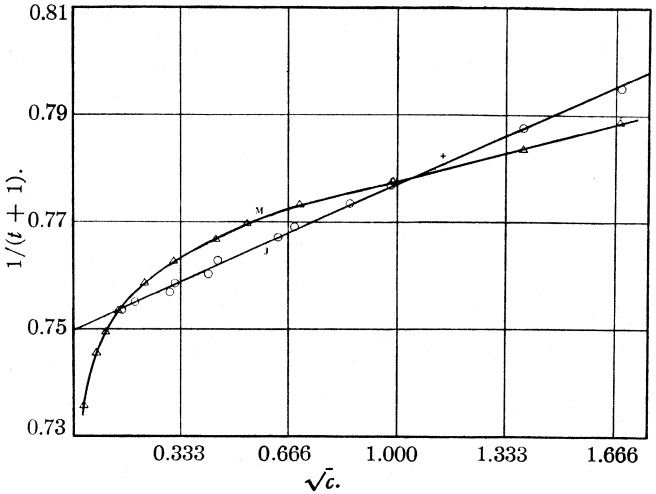


Fig. 2.—Transference number of the lithium ion in lithium chloride, $1/(t + 1)$ plotted against $\sqrt{c}$: △, Curve M, MacInnes and Beattie; ⊙, Straight line J, Jones and Bradshaw; +, Washburn.

At the time that this experimental work was started the moving boundary method had been much improved by MacInnes but its reliability had not been demonstrated completely by direct comparison with the analytical method, although MacInnes and Dole and Longsworth had kindly told us that they were engaged in making such a comparison. This work has since been completed brilliantly.[7] After making important improvements in the experimental details of both methods MacInnes and Dole and Longsworth have shown that the moving boundary method and the analytical method give identical results for potassium chloride within the concentration range 0.02 to 0.2 normal.

[5] J. Kuschel, *Wied. Ann. Physik*, **13**, 295 (1881); W. Bein, *Z. physik. Chem.*, **27**, 38 (1898); H. Jahn, *ibid.*, **37**, 691 (1901); J. N. Pearce and F. S. Mortimer, THIS JOURNAL, **40**, 509 (1918).

[6] Ref. 3, p. 1126.

[7] D. A. MacInnes and Malcolm Dole, THIS JOURNAL, **53**, 1357 (1931).

## Experimental Part

Lithium nitrate of good quality was dissolved in hot water and freshly distilled ammonium carbonate solution added. The precipitated lithium carbonate was washed repeatedly with hot water until free from nitrate as shown by testing with diphenylamine dissolved in concentrated sulfuric acid. The lithium carbonate was dissolved in redistilled hydrochloric acid and evaporated to dryness, then redissolved in water and evaporated to dryness several times to remove excess of acid. The resulting salt gave a neutral solution and is believed to have contained no impurity in significant amounts except water.

The apparatus and procedure were essentially the same as that described by Washburn[4] with the modifications given by Jones and Dole and hence need not be described in detail. All measurements were carried out at 25 ± 0.02°. Concentrations are expressed in gram molecules per liter.

Table I gives the fundamental experimental data for all successful experiments and the transference numbers computed from these data. It will be noted that the greatest difference between the results at the anode and at the cathode is only 0.0006 and the average difference is less than 0.0002.

In addition to these successful experiments there were about an equal number which failed for one reason or another. In some cases there was evolution of gas at one or both electrodes due to the use of too high a current or to the continuation of the experiment for too long a time so that the effective capacity of the electrodes was exceeded. In some cases when working with the more dilute solutions colloidal silver chloride appeared in the solution around the anode and fell through the solution, causing stirring. Several experiments had to be rejected because the results from the anode and cathode did not agree, which may have been due to some error in the analysis. The most dilute solution for which we succeeded in obtaining a trustworthy result was 0.023 normal. Several attempts were made to obtain results with a 0.01 normal solution but these failed owing to the appearance of colloidal silver chloride at the anode and to the fact that the amount of lithium chloride transferred was so small that sufficient precision could not be obtained in the analysis.

With 2 *N* and 3 *N* solutions the amount of lithium chloride which can be transferred is such a small fraction of the amount originally present that its determination with sufficient precision is difficult. Moreover, in these strong solutions silver chloride dissolves with the formation of a complex ion[8] in an appreciable amount and must introduce some error. These strong solutions were always diluted as the first step in the analysis, this causing the precipitation of a small amount of silver chloride, which was filtered out, and then the filtrate was treated with silver nitrate solution and the silver chloride thus formed collected and weighed. By this pro-

[8] G. S. Forbes, THIS JOURNAL, **33**, 1937 (1911).

TABLE I

EXPERIMENTAL DATA

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Concn., moles per liter | 0.023243 | 0.037011 | 0.090633 | 0.101135 | 0.17840 | 0.20217 | 0.40444 | 0.47301 | 0.73453 | 0.96562 | 1.91578 | 2.95322 |
| Density | .99766 | .99801 | .99944 | .99963 | 1.00153 | 1.00213 | 1.00723 | 1.00873 | 1.01498 | 1.02049 | 1.04229 | 1.06464 |
| Amperes | | .012 | .025 | .03 | 0.03 | 0.05 | 0.05 | 0.055 | 0.1 | 0.1 | 0.07 | 0.2–0.1 |
| Volts | | 70 | 70 | 69 | 55 | 70 | 41 | 35 | 50 | 40.5 | 17 | 30–13 |
| Hours of electrolysis | | 8 | 6 | 8 | 4 | 7 | 8 | 6 | 7 | 6 | 7 | 7 |
| Ag in coulometers, g. | 0.20865 | 0.30802 | 0.57585 | 0.73935 | 0.51677 | 1.37588 | 1.43908 | 1.27409 | 2.03070 | 2.44671 | 2.00121 | 4.83599 |
| | | | 0.57588 | 0.73937 | 0.51682 | 1.37587 | 1.43902 | 1.27409 | 2.03081 | | 2.00120 | 4.83600 |
| Middle portion, mg. LiCl per g. $H_2O$ | 0.98977 | 1.5762 | 3.8643 | 4.3124 | 7.6176 | 8.6356 | 17.337 | 20.305 | 31.686 | 41.838 | 84.604 | 133.428 |
| Weight anode portion, g. | 126.775 | 127.002 | 123.340 | 128.615 | 128.135 | 124.894 | 122.740 | 129.529 | 124.017 | 132.90 | 124.224 | 121.497 |
| Mg. LiCl per g. $H_2O$ anode | 0.77707 | 1.2685 | 3.3043 | 3.5941 | 7.1141 | 7.2899 | 15.923 | 19.126 | 29.754 | 39.678 | 82.7655 | 128.937 |
| Mg. LiCl transferred from anode | 26.688 | 39.033 | 72.19 | 92.053 | 64.059 | 166.85 | 170.83 | 149.85 | 232.68 | 276.11 | 210.93 | 483.32 |
| Corr. for LiCl trans. from anode middle | 0.143 | 0.258 | 0.46 | 0.505 | 0 | 1.29 | 0.96 | 0.44 | 0.98 | 0 | 1.02 | 6.38 |
| Total LiCl transferred from anode | 26.831 | 39.291 | 72.65 | 92.558 | 64.059 | 168.14 | 171.79 | 150.29 | 233.66 | 276.11 | 211.95 | 489.70 |
| Weight cathode portion, g. | 121.456 | 120.415 | 121.453 | 123.074 | 123.440 | 123.456 | 123.950 | 123.329 | 122.507 | 128.542 | 127.227 | 128.246 |
| Mg. LiCl per g. $H_2O$ cathode | 1.20939 | 1.9031 | 4.4626 | 5.0797 | 8.1409 | 10.0032 | 18.739 | 21.5465 | 33.652 | 44.143 | 86.410 | 137.743 |
| Mg. LiCl transferred to cathode | 26.642 | 39.289 | 72.34 | 92.429 | 64.075 | 167.16 | 170.58 | 149.94 | 233.01 | 276.16 | 211.50 | 486.39 |
| Corr. LiCl trans. to cathode middle | 0.179 | 0 | 0.32 | 0.775 | 0 | 0.97 | 0.92 | 0.40 | 0.71 | 0 | 0.68 | 2.68 |
| Total LiCl trans. to cathode mg. | 26.821 | 39.289 | 72.66 | 93.204 | 64.075 | 168.13 | 171.50 | 150.34 | 233.72 | 276.16 | 212.18 | 489.07 |
| Transference number anode | 0.3272 | 0.3246 | 0.3210 | 0.3185 | 0.3153 | 0.3109 | 0.3038 | 0.30015 | 0.2928 | 0.2871 | 0.2695 | 0.2577 |
| Transference number cathode | .3271 | .3246 | .3210 | .3184 | .3155 | .3109 | .3032 | .30025 | .2928 | .2872 | .2698 | .2573 |
| Accepted value | .3272 | .3246 | .3210 | .3184 | .3154 | .3109 | .3035 | .3002 | .2928 | .2872 | .2696 | .2575 |

cedure the dissolved silver chloride did not cause an error in the analysis directly although, of course, the extra filtration increased the danger of accidental errors. But the conversion of a part of the chloride into a complex ion must have a slight effect on the effective transference number of the chloride ion; and since there is some doubt as to the formula of the complex ion, its mobility is unknown and the amount present was small, no attempt has been made to apply a correction for this source of error. Since the proportion of the complex ion increases with the concentration, together with the fact that the measurements of MacInnes and Beattie do not extend beyond 3 normal, we made no attempt to make any measurements on still more concentrated solutions.

When these results are plotted as transference number, $t$, against the square root of the concentration, $\sqrt{c}$, a curve is obtained which is nearly but not quite straight, as is shown in Fig. 1, curve J. When $1/(t + 1)$ is plotted against $\sqrt{c}$, a straight line is obtained as is shown in Fig. 2, curve J. The equation of the best straight line through these twelve points was found by the method of least squares to be

$$\frac{1}{t + 1} = 0.74979 + 0.02703\sqrt{c} \qquad (3)$$

This may be readily transformed into

$$t = \frac{1.3337}{1 + 0.03605\sqrt{c}} - 1 \qquad (4)$$

Table II contains a comparison between the observed values of the transference number and the values computed for each concentration by this equation. The average deviation between the observed and computed values is less than 0.0010. Although these deviations are greater than had been found by Jones and Dole in the case of barium chloride, they are not systematic. Since we have fitted twelve points to a two parameter

TABLE II

TRANSFERENCE NUMBERS OF LITHIUM ION IN LITHIUM CHLORIDE AT 25°. COMPARISON OF OBSERVED VALUES AND VALUES COMPUTED BY EQUATION 4

| $c$ | $\sqrt{c}$ | $t$ obs. | $\frac{1}{t+1}$ | $t$ calcd. | $t$ obs. $-t$ calcd. |
|---|---|---|---|---|---|
| 0.023243 | 0.15246 | 0.3272 | 0.75347 | 0.3264 | +0.0008 |
| .037011 | .19238 | .3246 | .75495 | .3245 | + .0001 |
| .090633 | .30105 | .3210 | .75700 | .3194 | + .0016 |
| .101135 | .31802 | .3184 | .75849 | .3186 | − .0002 |
| .17840 | .42238 | .3154 | .76022 | .3137 | + .0017 |
| .20217 | .44963 | .3109 | .76283 | .3124 | − .0015 |
| .40444 | .63596 | .3035 | .76717 | .3038 | − .0003 |
| .47301 | .68776 | .3002 | .76911 | .3014 | − .0012 |
| .73453 | .85705 | .2928 | .77351 | .2937 | − .0009 |
| .96562 | .98266 | .2872 | .77688 | .2881 | − .0009 |
| 1.91578 | 1.38412 | .2696 | .78765 | .2703 | − .0007 |
| 2.95322 | 1.71851 | .2575 | .79522 | .2559 | + .0016 |

equation and the independent variable is varied over a 127-fold range, it seems probable that the equation is significant and useful for interpolation and for extrapolation to zero concentration. In Table III are given the values for the transference number of the lithium ion in lithium chloride solutions at 25° at round concentrations as computed by this equation, (4). The value for the transference number at infinite dilution extrapolated by this equation is 0.3337.

TABLE III

TRANSFERENCE NUMBERS OF THE LITHIUM ION IN LITHIUM CHLORIDE SOLUTIONS AT 25° AS COMPUTED FROM EQUATION 4

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $c$ | 0 | 0.001 | 0.002 | 0.003 | 0.005 | 0.01 | 0.02 | 0.03 |
| $t$ | 0.3337 | .3322 | .3316 | .3311 | .3303 | .3289 | .3269 | .3254 |
| $c$ | .05 | .1 | .2 | .3 | .5 | 1.0 | 2.0 | 3.0 |
| $t$ | .3230 | .3187 | .3125 | .3079 | .3006 | 0.2873 | 0.2690 | 0.2553 |

Our results for the density of lithium chloride solutions at 25° agree with the equation $d = 0.99707 + 0.02494\,c - 0.000698\,c^2$ (5)

**Reinterpretation of the Data of MacInnes and Beattie.**—MacInnes and Beattie have measured the electromotive force of concentration cells without transference of the type

$$\text{Ag, AgCl, LiCl}(c_2), \text{LiHg}_x \ldots . \text{LiHg}_x, \text{LiCl}(c_1), \text{AgCl, Ag}$$

and with transference of the type

$$\text{Ag, AgCl, LiCl}(c_2), \text{LiCl}(c_1), \text{AgCl, Ag}$$

over a range of concentration from 0.001 to 3.0 molal. The values of the transference numbers computed by these authors from their data are shown in Figs. 1 and 2 by points inside triangles and as will be seen are not in agreement with our results obtained by the analytical method, which are shown by the circles in the same figures.

We have, however, found that when these data are interpreted in a more rigorous manner, the computed transference numbers agree with our data much better.

The rigid differential equation for the electromotive force of a concentration cell with transference with electrodes reversible with respect to the anion is

$$dE = -\frac{2RT}{F} t\, d \ln a \qquad (6)$$

where $t$ is the transference number of the cation, $a$ is the geometric mean of the activities of the two ions and the other symbols have their usual significance.[9] In order to integrate this equation we need reliable expressions for the $t$ and $a$ as functions of the concentration.

[9] MacInnes and Beattie give this equation without the negative sign but since the cells under consideration are reversible with respect to the negative ion, increasing the concentration or the activity of the ions in the solution causes the electrode to become more negative and hence $dE/da$ should be negative.

At the time that the paper of MacInnes and Beattie was published (1920), the Debye-Hückel theory had not yet been proposed and no reliable expression for $t$ and $a$ as functions of the concentration was known. MacInnes and Beattie were, therefore, compelled to rely on empirical methods of integration and interpretation instead of analytical methods. The unavoidable errors in plotting plus the guesswork in drawing smooth curves through the experimental points may cause errors much greater than the experimental errors. MacInnes and Beattie reached the conclusion that the transference number of the lithium ion in lithium chloride is given by the expression

$$t = 0.3834 - 0.0259 \log A \quad (\text{where } A = a \times 10^4) \tag{7}$$

This expression may be readily transformed into

$$t = 0.28224 - 0.0259 \log a \tag{8}$$

As $c$ approaches zero, $a$ also approaches zero and $\log a$ approaches $-\infty$; hence equation (8) requires that $t$ approaches $+\infty$. This expression, therefore, gives an abnormally rapid rise in the transference number as the concentration approaches zero, as is shown in Fig. 1, and must therefore be incorrect. Jones and Dole have pointed out that the empirical method may now be advantageously replaced by a more rigid although more laborious algebraic method based on the equation of Hückel[10] for the variation of the activity coefficient with the concentration and the equation of Jones and Dole for the variation of the transference number with the concentration.

Hückel has derived the following equation for the activity coefficient as a function of the concentration

$$\log f = -\frac{0.354\sqrt{2c}}{1 + N\sqrt{c}} + Pc \tag{9}$$

where $N$ and $P$ are constants for any given salt and temperature and solvent, and he has cited evidence tending to show that unlike most of the equations derived from the interionic attraction theory, this equation is valid even up to 3 normal. The first step is therefore to determine the numerical values of $N$ and $P$ for lithium chloride at 25° from the data of MacInnes and Beattie on the electromotive force of concentration cells without transference. MacInnes and Beattie express their concentrations, $m$, in terms of moles per 1000 grams of water. We have found it more convenient to make the calculations in terms of moles per liter, $c$, and therefore have first computed the concentration of each of their solutions on this basis. MacInnes and Beattie do not give the densities of their solutions and we have therefore used our equation $d = 0.99707 + 0.02494\,c - 0.000698\,c^2$ for this purpose. It is convenient for the calculation to use the 3.0 molal solutions as a common reference solution. The

[10] E. Hückel, *Physik. Z.*, **26**, 93 (1925).

differential equation for the electromotive force of concentration cells without transference for a monovalent metal is

$$dE = -\frac{2RT}{F} d\ln a = -\frac{2RT}{F} 2.3026 d(\log c + \log f) =$$
$$-\frac{2RT}{F} 2.3026\, d\left(\log c - \frac{0.500632\sqrt{c}}{1 + N\sqrt{c}} + Pc\right) \quad (10)$$

This equation when integrated between the limits $c_2$ and $c_1$ gives

$$E_2 - E_1 = -5.6052 \frac{RT}{F}\left[\left(\log c_2 - \frac{0.500632\sqrt{c_2}}{1 + N\sqrt{c_2}} + Pc_2\right)\right.$$
$$\left. - \left(\log c_1 - \frac{0.500632\sqrt{c_1}}{1 + N\sqrt{c_1}} + Pc_1\right)\right] \quad (11)$$

For the details of the mathematical procedure by which $N$ and $P$ may be computed from the data by this equation we refer to the paper of Jones and Dole and give only the result that $N = 0.89055$ and $P = 0.15003$. The figures 5.6052 and 0.500632 are theoretical values not selected to fit the data.

$$\log a = \log c + \log f = \log c - \frac{0.500632\sqrt{c}}{1 + 0.89055\sqrt{c}} + 0.15003\, c \quad (12)^{11}$$

The results of these calculations are shown in Table IV.

TABLE IV

COMPARISON OF THE ELECTROMOTIVE FORCE OF LiCl CONCENTRATION CELLS WITHOUT TRANSFERENCE AS OBSERVED BY MACINNES AND BEATTIE WITH THE RESULTS COMPUTED BY EQUATION 10

| $m$ | $c$ | $\sqrt{c}$ | $E_m - E_{3.0}$, volts obs. | $E_m - E_{3.0}$, volts calcd. | $E$ obs. − calcd., volts |
|---|---|---|---|---|---|
| 3.0 | 2.8625 | 1.68121 | 0 | 0 | 0 |
| 1.0 | 0.97931 | 0.98960 | +0.07890 | +0.07853 | +0.00037 |
| 0.3 | .29754 | .54548 | + .14170 | + .14243 | − .00073 |
| .1 | .099533 | .31549 | + .19540 | + .19505 | + .00035 |
| .03 | .029896 | .17290 | + .25287 | + .25237 | + .00050 |
| .01 | .009969 | .099845 | + .30595 | + .30571 | + .00024 |
| .003 | .0029911 | .054691 | + .36562 | + .36535 | + .00027 |
| .001 | .00099705 | .031576 | + .41985 | + .42056 | − .00071 |
| | | | | $\Sigma\Delta E$ | + .00029 |

[11] Attention is called to an error in equation 12 of Jones and Dole, THIS JOURNAL, 51, 1085 (1929). In this equation the square root sign in the numerator should be deleted in two places so that the equation should read

$$\Delta E = -\frac{3 \times 2.3026\, RT}{2F}\left[\left(\frac{1.734\, c_2}{1 + N\sqrt{c_2}} - \frac{1.734\, c_1}{1 + N\sqrt{c_1}}\right)\Delta N + (c_2 - c_1)\Delta P\right]$$

This error is typographical only, as the correct form was used in the calculations whose results are recorded in the earlier paper. The above equation is applicable to a divalent–monovalent salt ($BaCl_2$). For a monovalent salt (LiCl) the factor 3/2 should be replaced by the factor 2 and the factor 1.734 by the factor 0.500632 so that the equation becomes

$$E = -\frac{2 \times 2.3026\, RT}{F}\left[\left(\frac{0.500632\, c_2}{(1 + N\sqrt{c_2})^2} - \frac{0.500632\, c_1}{(1 + N\sqrt{c_1})^2}\right)\Delta N + (c_2 - c_1)\,\Delta P\right]$$

The deviations are not systematic and in view of the fact that the independent variable ($c$) is varied over a range of 3000-fold, the agreement between the observed and computed results is good.

Having now found that

$$\ln a = \ln c + \ln f = 2.3026\,(\log c + \log f) = 2.3026\left(\log c - \frac{0.500632\sqrt{c}}{1 + N\sqrt{c}} + Pc\right) = 2.3026\left(\log c - \frac{0.500632\sqrt{c}}{1 + 0.89055\sqrt{c}} + 0.15003\,c\right) \quad (13)$$

from the data of MacInnes and Beattie on concentration cells without transference and

$$t = \frac{A}{1 + B\sqrt{c}} - 1 = \frac{1.3337}{1 + 0.03605\sqrt{c}} - 1$$

from our own data on transference numbers by the analytical method we may substitute these values in the fundamental differential equation

$$dE = -2\frac{RT}{F}\,t\,d\ln a \quad (6)$$

and integrate the resulting equation between the limits $c_2$ and $c_1$. $x$ is substituted for $\sqrt{c}$ as a matter of convenience in integration. The result

$$E_2 - E_1 = 0.118308\left[-\frac{2APx}{B} + Px^2 - (2A - 2)\log x + \left(\frac{2A}{2.3026} + \frac{0.500632AB}{(N - B)^2} + \frac{2AP}{B^2}\right) 2.3026\log(1 + Bx) - \left(\frac{0.500632A}{N - B} - \frac{0.500632}{N}\right)\frac{1}{1 + Nx} - \frac{0.500632AB \times 2.3026\log(1 + Nx)}{(N - B)^2}\right]_{x_1}^{x_2} \quad (14)$$

Then substituting the above indicated values for the constants this reduces to

$$E_2 - E_1 = \left[-1.313344x + 0.0177498x^2 - 0.078961\log x + 84.210421\log(1 + 0.03605x) - \frac{0.0259366}{1 + 0.89055x} - 0.0089803\log(1 + 0.89055x)\right]_{x_1}^{x_2} \quad (15)$$

$E_2 - E_1$ was then computed for each solution referred to the 3.0 molal solution as a standard of reference and the results are shown in Table V.

TABLE V

LITHIUM CHLORIDE CONCENTRATION CELLS WITH TRANSFERENCE AT 25°. COMPARISON OF MACINNES AND BEATTIE'S OBSERVED VALUES WITH VALUES COMPUTED BY EQUATIONS

| | | | | $A = 1.3337$, $B = 0.03605$ | | $A = 1.3394$, $B = 0.04565$ | |
|---|---|---|---|---|---|---|---|
| $m$ | $c_2$ | $\sqrt{c_2}$ | $E_2 - E_1$ volts, $c_1 = 3.0$ | $E_2 - E_1$ computed, volts | $\Delta E$ obs.−comp., volts | $E_2 - E_1$ computed, volts | $\Delta E$ obs.−comp. volts |
| 3.0 | 2.8265 | 1.68121 | 0 | 0 | 0 | 0 | 0 |
| 1.0 | 0.97931 | 0.98960 | +0.020561 | +0.021401 | −0.00084 | +0.020637 | −0.000076 |
| 0.3 | .29754 | .54548 | + .039575 | + .040490 | − .000915 | + .039483 | + .000092 |
| .1 | .099533 | .31549 | + .055989 | + .056973 | − .000984 | + .056015 | − .000026 |
| .03 | .029896 | .17290 | + .074786 | + .075469 | − .000683 | + .074650 | + .000136 |
| .01 | .009969 | .099845 | + .091878 | + .092915 | − .001037 | + .092320 | − .000442 |
| .003 | .0029911 | .054691 | + .112391 | + .112630 | − .000239 | + .112288 | + .000103 |
| .001 | .00099705 | .031576 | + .130934 | + .130919 | + .000015 | + .130885 | + .000049 |
| | | | | $\Sigma\Delta E = -0.004633$ | | $\Sigma\Delta E = -.000164$ | |

The significance of these data is best made clear by a consideration of Fig. 3, in which $E_2 - E_1$ is plotted against log $c_2$. This method of plotting was chosen because it gives a curve which is more nearly straight than any other method we have found but careful inspection shows that the curve is not straight but has a point of inflection near the middle with opposite curvature at the two ends. In Fig. 3 the observed values of MacInnes and

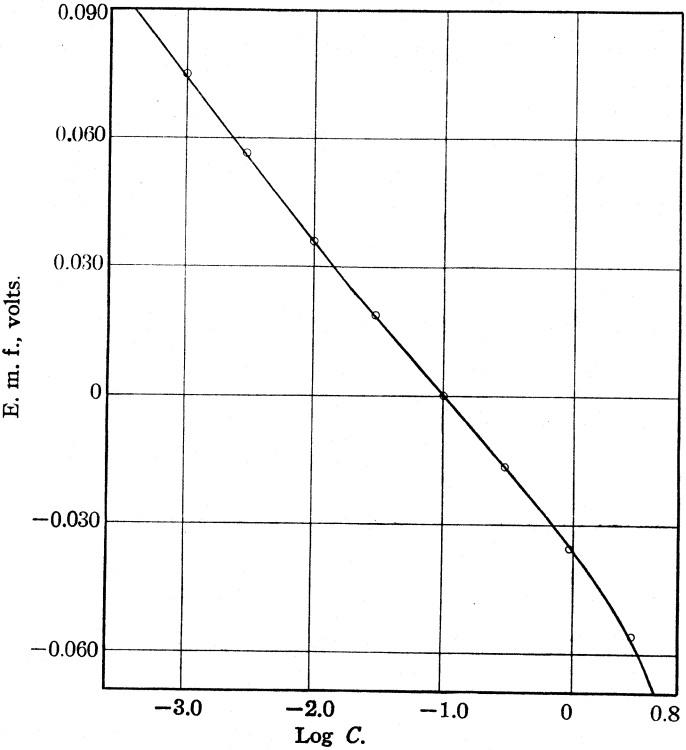


Fig. 3.—Electromotive force of lithium chloride concentration cells with transference, plotted against log $C_2$. Points inside circles represent experimental data of MacInnes and Beattie. The curve is the plot of equation (15).

Beattie are shown as points within the circles whereas the curve is the plot of the equation (15) and hence represents the value of the electromotive force of lithium chloride concentration cells with transference predicted from independent data, namely, our values of the transference numbers obtained by the analytical method and MacInnes and Beattie's determinations of the activities of the ions in lithium chloride by measurements of the electromotive force of concentration cells without transference. As will be seen from Fig. 3 the experimental values of the electromotive force of concentration cells with transference fit the computed curve closely

and follow the complicated curvature throughout the range. This shows that there is no real discrepancy between our results for the transference number of lithium chloride obtained by the analytical method and the data of MacInnes and Beattie. The apparent discrepancy depicted in Figs. 1 and 2 is therefore due to faulty computation of transference numbers by MacInnes and Beattie from their data. This case is in every respect analogous to the case of barium chloride discussed in an earlier paper by Jones and Dole and therefore furnishes additional evidence as to the general validity of the equation

$$t = \frac{A}{1 + B\sqrt{c}} - 1$$

But although the deviations between the observed and the computed values are so small as to be scarcely visible on a 50-cm. plot, the computations recorded in Table V show that there are deviations which are apparently systematic and somewhat larger than the probable experimental errors. We may, therefore, reverse the calculations and compute transference numbers from the data of MacInnes and Beattie using the assumption that the equation expressing the variation of the transference number with the concentration will have the form of the Jones and Dole equation and determine the values for the constants in this equation from the electromotive force data alone. The mathematical procedure for doing this has been explained in detail in the paper of Jones and Dole and will not be repeated here. The computations required are extremely laborious. However the fundamental differential equation for the electromotive force of concentration cells with transference is integrated and applied without introducing any mathematical assumptions or premises other than the Hückel activity function and the Jones and Dole transference function. The result of these calculations is $A = 1.3394$ and $B = 0.04565$.

The values for the electromotive force of concentration cells with transference were computed with these values of $A$ and $B$ and the results are shown in the last two columns of Table V. As will be seen, the deviations between the observed and computed values are small. The sum of all the deviations is $-0.00016$ volt and the average deviation disregarding the sign is 0.00013 volt.

We may conclude, therefore, that the data of MacInnes and Beattie may be interpreted as showing the transference number of lithium chloride to be $t = [1.3394/(1 + 0.04565\sqrt{c})] - 1$.

This equation leads to a value for the transference number at infinite dilution of 0.3394 instead of 0.3337 obtained by extrapolation from the analytical data. As the concentration is increased, the difference between the results of the two methods decreases up to 0.2 normal, where the results differ by only 0.001, and then the sign of the difference is reversed at higher concentrations and becomes $-0.0064$ at 1 normal and $-0.014$ at 3

normal. These differences are believed to be due to experimental errors in one or both sets of experimental data. We conclude that the data of MacInnes and Beattie when interpreted with the aid of Hückel's equation for the activity coefficient support the Jones and Dole equation for the variation of transference numbers with the concentration.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for the expenses of this investigation.

## Summary

1. The transference numbers of the lithium ion in lithium chloride solutions have been measured by the analytical method at 25° at many different concentrations between 0.023 and 2.95 normal and found to vary from 0.3272 to 0.2575 over this range.

2. The results can be expressed by the equation

$$t = [1.3337/(1 + 0.03605\sqrt{c})] - 1$$

3. The limiting value of the transference number of the lithium ion in lithium chloride at 25° is 0.3337.

4. It is computed from the data of MacInnes and Beattie on the electromotive force of concentration cells without transference that the mean activity coefficient of the ions in lithium chloride at 25° varies with the concentration in accordance with the equation

$$\log_{10} f = [-0.500632\sqrt{c}/(1 + 0.89055\sqrt{c})] + 0.15003\,c$$

This function has the form derived by Hückel.

5. The data of MacInnes and Beattie on the electromotive force of lithium chloride concentration cells with transference when interpreted by the method of Jones and Dole lead to the conclusion that the transference number is $t = [1.3394/(1 + 0.04565\sqrt{c})] - 1$.

6. The equation for the transference number of the cation as a function of the concentration $t = [A/(1 + B\sqrt{c})] - 1$, which Jones and Dole have shown to be valid for barium chloride is proved in this paper to be valid for lithium chloride also.

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# THE DENSITY AND MOLECULAR STATE OF THE VAPORS OF TELLURIUM DIBROMIDE, TELLURIUM TETRABROMIDE AND SELENIUM DIOXIDE

BY DON M. YOST AND JOHN B. HATCHER

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## Introduction

Earlier investigations on tellurium tetrabromide by those interested in atomic weight determinations[1] indicated that at higher temperatures the decomposition into the dibromide and bromine is appreciable; but the extent of this decomposition, with all the substances in the vapor phase, has not been studied. Such studies have been made on selenium tetrachloride[2] and tetrabromide[3] and they were found to be completely decomposed, in the vapor phase, into the dihalide and halogen. It has recently been established by Simons[4] that tellurium tetrachloride undergoes no appreciable decomposition up to 500°, beyond which the dissociation into the dichloride and chlorine increases with the temperature. It was considered of interest to extend these studies to the tellurium bromides, and thus complete this phase of the chemistry of these substances.

The vapor-pressure measurements carried out by J. Meyer and Jannek[5] on selenium dioxide in the temperature range 70 to 320° yielded results which indicate that the vapor may be more or less polymerized. The only existing value for the vapor density is one made some time ago by Mitscherlich[6] who did not give the temperature of the experiments and which is too inaccurate to permit any decision to be made concerning any possible polymerization.

In this paper are presented the results of experiments made on tellurium dibromide and tetrabromide over the range of temperatures from 440 to 1000°, together with the results obtained for the vapor density of selenium dioxide between 350 and 500°.

## Experimental Procedure and Preparation of the Materials

The vapor densities were determined by the Dumas method, using the procedure described in a former paper.[3] This procedure consists in heating to a definite temperature a tube of known volume containing accurately

[1] *Cf.* Abegg, Auerbach and Koppel, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, **1927**, Vol. IV, Part 1, Section 1, pp. 812, 894.

[2] Yost and Kircher, THIS JOURNAL, **52**, 4680 (1930).

[3] Yost and Hatcher, *ibid.*, **53**, 2549 (1931).

[4] Simons, *ibid.*, **52**, 3488 (1930).

[5] Jul. Meyer and Jannek, *Z. anorg. Chem.*, **83**, 62 (1913).

[6] E. Mitscherlich, *Ann. chim. phys.*, [2] **55**, 5 (1833).

weighed portions of tellurium and bromine only and subsequently allowing the excess of vapor to escape until the contents of the tube are at atmospheric pressure. In the case of the selenium dioxide experiments, the hydrated material was introduced into a tube of known weight and volume, the material was carefully dried by heating while under a vacuum, and the tube was subsequently sealed off and again weighed, the difference in the weight being the weight of selenium dioxide. For the experiments carried out above 600° quartz tubes were used. At temperatures above 1000° appreciable errors may arise as a result of losses in the weights of the quartz tubes. The temperatures were measured by means of a chromel–alumel thermocouple which had been carefully calibrated.

The bromine used was prepared and purified in the manner described elsewhere.[3] A commercial grade of metallic tellurium which contained copper and selenium was carefully purified using the method described in detail by Schuhmann.[7]

Selenium dioxide was prepared as follows. Carefully purified selenium[2] was treated with concentrated nitric acid, the resulting solution of selenious acid was evaporated to dryness, the residue redissolved in water and the solution was filtered and again evaporated to dryness. The resulting material was then sublimed and only those portions free from color were used for filling the vapor-density tubes.

**Results of the Tellurium Bromide Experiments.**—In Table I are presented representative results selected from the thirty vapor-density measurements made on tellurium dibromide and tetrabromide. The values for the apparent molecular weight $M$ given in the last column of the table were calculated from the formula $M = 760 \times 82.07mT/pv$, where $m$ is the mass of material in grams remaining in the tube at the absolute temperature $T$ and barometric pressure $p$ (in millimeters), and $v$ the volume of the tube in cubic centimeters. It is assumed, of course, that the vapor obeys the perfect gas laws. The initial amounts of dibromide and tetrabromide in the tubes varied from 0.2491 to 0.6584 g.

As may be seen from the table, the molecular weight of tellurium dibromide is, within the limits of experimental error (±2%), the same as its formula weight up to a temperature of approximately 750°. Above this temperature the values are definitely lower, thus indicating decomposition into tellurium and bromine. Owing to the fact that the errors involved at the higher temperatures are appreciable, it was not thought significant to carry out any thermodynamical calculations using these results. For the same reason no corrections were made for the dissociation of bromine.

The color of the solid dibromide is black, and that of the vapor below 650° is violet and closely resembles that of iodine vapor. At higher temperatures the color of the gas shades from reddish brown to salmon

[7] Schuhmann, THIS JOURNAL, 47, 356 (1925).

TABLE I

VAPOR DENSITIES OF TELLURIUM DIBROMIDE AND TETRABROMIDE

Formula weight of $TeBr_2$, 287.34 Formula weight of $TeBr_4$, 447.17

| Experiment | Compound | Material left in tube, $m$, g. | Barometric pressure, $p$, mm. | Vol. tube $v$ in cc. | Temp., °C. | Molecular weight $M$, calcd. |
|---|---|---|---|---|---|---|
| 1 | $TeBr_2$ | 0.1921 | 741.5 | 41.4 | 458 | 285 |
| 3 | $TeBr_2$ | .1744 | 741.5 | 41.4 | 533 | 286 |
| 5 | $TeBr_2$ | .1704 | 740.0 | 46.3 | 640 | 283 |
| 6 | $TeBr_2$ | .1330 | 740.0 | 46.3 | 883 | 280 |
| 7 | $TeBr_2$ | .1191 | 742.0 | 46.3 | 950 | 264 |
| 8 | $TeBr_2$ | .1029 | 742.0 | 46.3 | 1013 | 240 |
| 20 | $TeBr_4$ | .1703 | 740.0 | 42.2 | 432 | 240 |
| 9 | $TeBr_4$ | .1688 | 741.5 | 42.9 | 444 | 238 |
| 26 | $TeBr_4$ | .1590 | 739.4 | 41.2 | 470 | 242 |
| 29 | $TeBr_4$ | .1503 | 739.4 | 41.8 | 500 | 235 |
| 10 | $TeBr_4$ | .1498 | 741.5 | 42.9 | 505 | 229 |
| 16 | $TeBr_4$ | .1373 | 741.5 | 40.8 | 541 | 231 |
| 30 | $TeBr_4$ | .1331 | 739.4 | 41.8 | 578 | 229 |
| 12 | $TeBr_4$ | .1311 | 741.5 | 42.9 | 595 | 224 |
| 32 | $TeBr_4$ | .1417 | 740.0 | 48.3 | 620 | 221 |
| 33 | $TeBr_4$ | .1041 | 739.4 | 48.3 | 930 | 219 |
| 34 | $TeBr_4$ | .0995 | 742.0 | 48.3 | 997 | 220 |
| 35 | $TeBr_4$ | .0844 | 742.0 | 48.3 | 1034 | 192 |

pink, the lighter color occurring at the higher temperatures. It must be pointed out, however, that this change in color does not in itself necessarily show the formation of a new compound.

Independent observations on more dilute vapor at 300° with a visual spectrometer showed that the gas possesses a banded absorption spectrum stretching from the region 6700 to 5300 Å. It was found by Professor R. M. Badger of this Institute, with the aid of a grating spectrograph of large dispersion, that these bands possess no observable fine structure.

In the case of tellurium tetrabromide, the dissociation into the dibromide and bromine is quite extensive, even at the lowest temperature of 432°, where it amounts to more than 90%. At about 600° the dissociation is practically complete, and the calculated molecular weight $M$ is, within the limits of experimental error (±2%), one-half the formula weight. Further decomposition into tellurium and bromine does not take place to an appreciable extent at temperatures lower than 1000°, as is shown by the fact that the molecular weights remain nearly constant up to this point. This behavior is in complete accord with the greater decomposition of the dibromide at the higher temperatures and the mass action law, since the partial pressure of bromine in the tetrabromide experiments is much greater. The decomposition in both cases may be represented by the chemical equations

$$TeBr_4\,(g) = TeBr_2\,(g) + Br_2\,(g) \quad (1)$$

$$TeBr_2\,(g) = \tfrac{1}{2}Te_2\,(g) + Br_2\,(g) \quad (2)$$

The vapor pressure of tellurium at 750°[8] is sufficient to exclude the possibility of the presence of liquid tellurium.

The results given do not exclude the possibility of a decomposition at the lower temperatures taking place with the formation of the unknown tellurium monobromide, $Te_2Br_2$, and bromine in accordance with the chemical equations

$$2TeBr_4 = Te_2Br_2 + 3Br_2 \quad (3)$$
$$2TeBr_2 = Te_2Br_2 + Br_2 \quad (4)$$

That tellurium dibromide does not decompose to form the monobromide and bromine is shown by the fact that no bromine bands were observed in its absorption spectra. From this it appears that a mixture of the monobromide and bromine is not stable with respect to the formation of the dibromide, and hence the products of reaction (3) could not exist as such. It may be concluded, therefore, that the dibromide vapor is normal and that the tetrabromide decomposes to form the dibromide and bromine. It is assumed of course that all reactions come rapidly to equilibrium, and this assumption is probably correct since the temperatures involved are rather high.

At temperatures above 650° the color of the tetrabromide vapor is, to the eye, the same as that observed in the case of the dibromide at the same temperature. At lower temperatures the vapor has a reddish brown color, and on solidifying there results first dark orange crystals which become bright yellow at some point below 100°.

## Results of the Selenium Dioxide Experiments

The vapor densities of selenium dioxide over the range of temperatures from 360 to 500° are given in Table II. The initial amounts of selenium dioxide used varied from 0.1994 to 0.3189 g. As may be seen from the last column of the table, the values of the molecular weights, calculated as before, are, within the limits of experimental error (±1%), the same as the formula weight. It is clear from this that there is no appreciable polymerization of selenium dioxide vapor in this temperature range. If, then, the abnormal character of the vapor pressure curve is due to polymerization,

TABLE II

VAPOR DENSITIES OF SELENIUM DIOXIDE

Formula weight of $SeO_2$, 111.2

| Experiment | Material left in tube, $m$, g. | Barometric pressure, $p$, mm. | Vol. of tube, $v$ in cc. | Temp., °C. | Molecular weight $M$, calcd. |
|---|---|---|---|---|---|
| 3 | 0.0852 | 742.5 | 40.7 | 359 | 111 |
| 4 | .0817 | 742.5 | 40.7 | 400 | 114 |
| 1 | .0785 | 743.6 | 41.2 | 426 | 112 |
| 5 | .0708 | 742.5 | 40.7 | 496 | 112 |
| 2 | .0705 | 742.5 | 41.2 | 500 | 111 |

[8] Doolan and Partington, *Trans. Faraday Soc.*, **20**, 342 (1924).

the present results show that this effect can be appreciable only at the lower temperatures.

Independent experiments were made on the color of selenium dioxide vapor, these being carried out at 400° in a series of three tubes having a volume of 56.5 cc. and containing 0.1370 g. of selenium dioxide each. Oxygen at pressures of 0, 100 and 330 mm., respectively, was introduced in order to repress the formation of any free selenium or oxides containing more selenium than the dioxide. So far as could be determined visually, there was no marked difference either in the shade or intensity of the color in any of these tubes. Moreover, the color of the vapor in the vapor-density experiments was essentially that observed in these independent experiments. These results show that the color is not due, as has been suggested (*Cf.* Ref. 1, p. 733), to free selenium, a molecule containing more than one atom of selenium, a lower oxide, nor a polymerized molecule. The color of the vapor is green-yellow; and on cooling, white feathery crystals are deposited on the sides of the tubes.

## Summary

The vapor densities of tellurium dibromide and tetrabromide have been determined over the range of temperatures from 440 to 1000°. The dibromide vapor was found to be normal up to about 750°; but above this temperature appreciable dissociation into tellurium and bromine sets in. The tetrabromide is more than 90% decomposed at the lowest temperature (432°) into the dibromide and bromine, and complete dissociation into these substances is reached at about 600°. Appreciable dissociation of the resulting dibromide into tellurium and bromine does not take place until a temperature of about 1000° is reached.

Vapor-density determinations on selenium dioxide showed its vapor to be normal over the temperature range 360 to 500°. Observations on the color at these temperatures, in the absence and presence of oxygen, showed that the color is not due to elementary selenium, to a polymerized molecule, to a lower oxide, nor to a molecule containing more than one atom of selenium.

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[CONTRIBUTION FROM THE U. S. BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.]

# THE DISSOCIATION OF OZONE AND THE MECHANISM OF ITS THERMAL DECOMPOSITION

BY OLIVER R. WULF

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From the temperature coefficients of thermal ozone decomposition measured in their work, Wulf and Tolman[1] in 1927 computed the heat of dissociation of oxygen. To make this computation it was necessary to assume that the mechanism of the decomposition was of such a nature that the apparent heat of activation was the heat of dissociation of ozone into molecular and atomic oxygen. Completion of the decomposition was taken to be the reaction of oxygen atom with ozone molecule. This calculation involved, besides the apparent heat of activation, the thermochemically observed value for the heat of transformation of ozone into molecular oxygen. The heat of dissociation of oxygen thus computed was 128,000 calories, while the correct value has recently been shown[2] to be 117,000 calories. A combined uncertainty of about 6,000 calories in the determination of the heat of decomposition of ozone into molecular oxygen and of the heat of dissociation of ozone as determined from the temperature coefficient of this thermal decomposition, would bring these values into agreement, and it will be pointed out later that the assumed mechanism represents a sort of limiting case, the observed heat of activation being in general probably somewhat greater than the heat of dissociation of ozone if this mechanism does obtain.

The mechanism considered here is described in the equations

| | |
|---|---|
| $O_3 \rightleftharpoons O_2 + O$ | Approximate equilibrium slightly displaced by utilization of O. $\Delta H$ = 24,000 calories. |
| $O_3^* + O \longrightarrow 2O_2$ | where $O_3^*$ takes account of the circumstance that normal ozone molecule may require some activation. |

Much work has been done on this reaction with considerable disagreement in the results,[3] and some differences of opinion have been held as to the

[1] Wulf and Tolman, THIS JOURNAL, **49**, 1650 (1927).

[2] Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926). Birge, *Trans. Faraday Soc.*, **XXV**, 707 (1929). Frerichs, *Phys. Rev.*, **36**, 398 (1930).

[3] Warburg, *Ann. Physik*, **9**, 1286 (1902); Clement, *ibid.*, **14**, 341 (1904); Jahn, *Z. anorg. Chem.*, **48**, 260 (1906); Clarke and Chapman, *J. Chem. Soc.*, **93**, 1638 (1908); Perman and Greaves, *Proc. Roy. Soc.* (*London*), **80A**, 353 (1908); Chapman and Jones, *J. Chem. Soc.*, **97**, 2463 (1910); Griffith and McKeown, *ibid.*, **127**, 2086 (1925); Griffith and McKeown, *Z. physik. Chem.*, [A] **120**, 236 (1926); Belton, Griffith and McKeown, *ibid.*, **129**, 3153 (1926); Wulf and Tolman, THIS JOURNAL, **49**, 1183 (1927); **49**, 1202 (1927); **49**, 1650 (1927); Griffith and McKeown, *ibid.*, **49**, 2721 (1927); Riesenfeld and Bonholtzer, *Z. physik. Chem.*, [A] **130**, 241 (1927); Riesenfeld and Schumacher, *ibid.*, [A] **138**, 268 (1928); Riesenfeld and Wasmuth, *ibid.*, [A] **143**, 397 (1929); Schumacher and Sprenger, *ibid.*, [B] **6**, 446 (1930).

relative importance of the results. At this point, therefore, the author wishes to state explicitly the purpose of the present paper. It is not to give further review nor to discuss the merits of past work, but rather to give independent evidence which makes it seem probable that oxygen atoms are operative in thermal ozone decomposition for low concentration ozone in ozonized oxygen at one atmosphere pressure. These were the conditions under which Wulf and Tolman made their temperature coefficient measurements. Their work used the dynamic or flow method, a linear dependence of the logarithm of the specific second order rate on the reciprocal temperature was found, and the second order character of the reaction was also observed during the experiments.

The approximate agreement of the computed heat of dissociation of oxygen with the known value is suggestive. The authors continued in their 1927 work by investigating the kinetics of the second step in the mechanism, assuming that the concentration of oxygen atoms was practically the equilibrium concentration in the first step, to see whether or not the possible over-all rate of reaction was sufficiently large to account for the known rate of decomposition. To do this it was necessary to make detailed calculations of the thermodynamic quantities involved in the equilibrium represented in the first step. They found that there were not nearly sufficient collisions between oxygen atoms and ozone molecules to account for the observed rate. To make these calculations, Wulf and Tolman used the thermodynamic data available, even though some of these were not all that might be desired.

Somewhat later Professor W. F. Giauque very kindly pointed out that the value for the entropy of ozone, $S^{\circ}_{273}$ ($O_3$) = 86.5, resulting from the calculations (see equation 23, Ref. 1) was probably wrong, being much too high, and, furthermore, that a fair estimate could be made of this quantity from entropies already known. The author is much indebted to Professor Giauque for these remarks, which formed the starting point of the present paper. The location of the chief source of difficulty was not hard to place. It probably lies in the value for $\Delta F^{\circ}_{273}$ ($O_3 \longrightarrow 3/2\ O_2$), a quantity the experimental determination of which is very difficult. The estimation of the entropy of ozone can, however, be made with fair assurance within a few entropy units. To do this the author has compared the entropies of four triatomic molecules which are quite similar in certain respects to ozone. Their entropies are either given or readily computed from data that are at hand, and in these four cases the material has been taken from Lewis and Randall.[4] These molecules, their respective entropies so derived and their molecular weights are as follows

[4] Lewis and Randall, "Thermodynamics," McGraw Hill Book Co., New York, 1923.

| | |
|---|---|
| $CO_2$ (g), $S^\circ_{298} = 49.4$ | M. w. = 44 |
| $NO_2$ (g), $S^\circ_{298} = 53.7$ | M. w. = 46 |
| COS (g), $S^\circ_{298} = 52.4$ | M. w. = 60 |
| $SO_2$ (g), $S^\circ_{298} = 57.0$ | M. w. = 64 |

From inspection of these values surely a fair estimate of the entropy of $O_3$, M. w. = 48, can be made, reasonable limits being from 50 to 55 entropy units. In order to have some explicit basis for computing this quantity, however, the author has used an extension of the empirical formula suggested by Eastman[5] for the entropy of diatomic molecules, taking the entropy of triatomic molecules to be given by the expression

$$S^\circ_{298} = 3/2\ R \ln (A_1A_2A_3) + \text{constant}$$

and has determined the constant from the entropies of these four triatomic molecules as having the value 27.9. Computing the entropy of ozone from this formula one finds $O_3$ (g) $S^\circ_{298} = 52.6$. Without repeating in detail any of the calculations here, but following them through exactly as done in reference (1) except for this new value for the entropy of $O_3$, one finds an equilibrium constant for the first step of the mechanism described above very nearly the value necessary to give a concentration of oxygen atoms just that required by this mechanism; that is, the number of collisions between O and $O_3$ is then approximately equal to the observed second order rate. In particular the value for $\Delta F_{373}$ in equation 25 of reference (1) is equal to 19,100 calories and (for the same conditions as in Ref. 1) the partial pressure of oxygen atoms $3.3 \times 10^{-13}$ atm. This gives a number of collisions between O and $O_3$ of about $1.5 \times 10^{15}$ per cc. per second, while the number of molecular reactions occurring under the same conditions was $1.2 \times 10^{14}$ per cc. per second, thus reversing the conclusion from the calculations in Reference 1, there being ample collisions to account for the observed rate. It is evident, however, that if further activation were required in the over-all reaction, as for instance of $O_3$ in the second step in order that it might react with O, the correct value for the change in heat content $\Delta H$ in the first step to use in computing the equilibrium concentration of oxygen atoms, would not be that calculated from the heat of activation, since this, because of the additional activation, would yield a value greater than the heat of dissociation of ozone. Rather, the heat of dissociation of ozone itself should be used, and as has been pointed out above, this can be independently computed now from the heat of dissociation of oxygen, having the value of approximately 24,000 calories, a somewhat smaller value indeed than that computed from the temperature coefficient. With this we find a value for $\Delta F_{373}$ in equation (25) of 12,800 calories and the partial pressure of oxygen atoms equal to $1.6 \times 10^{-9}$ atm. This gives approximately $7 \times 10^{18}$ collisions per cc. per second between O and $O_3$, while, as was

[5] Lewis and Randall "Thermodynamics," p. 462.

mentioned above, the decomposition rate was $1.2 \times 10^{14}$ reactions per cc. per second, thus over $10^4$ more collisions than reactions. From a study of Kistiakowsky's results on the photochemical decomposition of ozone, Schumacher[6] has recently concluded that normal oxygen atoms react with ozone molecules about once in every 2000 collisions. The present treatment found from a calculation of the concentration of oxygen atoms in equilibrium with ozone molecules and oxygen molecules over $10^4$ more collisions between oxygen atoms and ozone molecules than were necessary to account for the thermal rate of decomposition. Thus, assuming that Schumacher's conclusion is justified, our calculation might be taken as indicating that the thermal decomposition actually does proceed through the interaction of oxygen atoms with ozone molecules.

A consideration of the general mechanism upon which these calculations have been based and which is illustrated in the above equations shows that at least two factors might, consistent with the principle of this mechanism, lead to a larger value for the heat of activation in reality than the heat of dissociation of ozone into $O_2$ and O. In the first place, the first of the two reactions represented in this equilibrium may require some activation. Whereas for true thermal equilibrium in the first step the apparent heat of activation of ozone decomposition would still appear, in spite of this consideration, to be exactly the heat of dissociation of ozone, nevertheless with reaction actually occurring and with conditions at some unknown distance from equilibrium in the first step, the apparent heat of activation for ozone would rise, tending toward the heat of dissociation of ozone plus the additional activation required in the forward reaction of the first step. However, while this may be important where the absolute rate is high, it does seem that at high total pressures and at the lowest ozone concentrations that have been studied, where the absolute rate is low, there is presumably sufficient time for the practical establishment of thermodynamic equilibrium in the first step, and hence this source of increase of the heat of activation over that of the heat of dissociation does not seem probable in the measurements of Wulf and Tolman. Secondly, however, the second step may require activation. In particular it would seem not improbable that the ozone molecule, normally possessing no unpaired electrons,[7] would require activation before it would enter into reaction with an oxygen atom. As was shown above, this is quite in accord with the calculations, one interpretation of which would be that only one in about every $10^4$ ozone molecules reacts with

[6] Schumacher, THIS JOURNAL, **52**, 2377 (1930).

[7] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, **1923**, pp. 130, 147, *et seq.*; *Chemical Reviews*, **1**, 234 (1924); Wulf, *Proc. Nat. Acad. Sci.*, **13**, 744 (1927); Vaidyanathan, *Indian J. Phys.*, **2**, 422 (1928).

an oxygen atom upon collision. The author believes that in the present state of our knowledge it is expedient to consider such a required activation as involving an alteration in the electronic structure of the molecule. Recent work on the absorption spectrum of ozone carried out in long paths by the author[8] has shown that there is a low-lying electronic level in this molecule somewhere below 1.2 volts, which conceivably represents this reactive state required for the ozone molecule by the above considerations, although it is obvious that one cannot obtain a very close check upon this at present. But from energy considerations it remains that the observed rate of ozone decomposition can be described by the suggested mechanism, the concentration of oxygen atoms in equilibrium with ozone molecule and oxygen molecule being ample, the ozone molecule apparently requiring certain energy of activation before it can react with an oxygen atom.

Thus, summarizing the above considerations, the calculations of the heat of dissociation of oxygen made by Wulf and Tolman in 1927 from their data on the temperature coefficient of thermal ozone decomposition yielded a value in fair agreement (actually somewhat high) with the correct value now known from other sources. The mechanism of ozone decomposition assumed in these calculations, besides including a reasonable explanation of the somewhat high calculated value for the heat of dissociation of oxygen, is found to yield a rate of decomposition which is in good agreement with the observed rate, when a reasonable value for the entropy of ozone is used. This is shown to constitute evidence that a form of this mechanism is the chief process by which ozone decomposes at one atmosphere pressure and low ozone concentrations. Such a mechanism would represent a particularly simple case of thermal temperature coefficient. However, the sensitiveness of the strongly exothermic ozone decomposition to impurities makes it a difficult reaction to observe kinetically free of disturbances. In conclusion, it may lend emphasis to state the above in a somewhat different order. If normal oxygen atoms react with ozone molecules as frequently as once in every $10^4$ collisions, then the use of our present knowledge of the heat of dissociation of oxygen leads to a concentration of oxygen atoms in equilibrium with ozone and oxygen which indicates that, for low rates and high total pressures, the reaction of oxygen atoms with ozone molecules is probably the principal cause of thermal ozone decomposition.

WASHINGTON, D. C.

[8] Wulf, *Proc. Nat. Acad. Sci.*, **16**, 507 (1930).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

# PHOTOCHEMICAL STUDIES. XIII. THE PHOTOCHEMICAL REACTION BETWEEN CHLORINE AND BENZENE IN THE GASEOUS PHASE[1]

BY CHARLES E. LANE, JR., AND W. ALBERT NOYES, JR.

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The photochemical reaction between chlorine and benzene in the liquid phase or in solution has been the subject of previous investigations. A complete bibliography of this work need not be given at this time.[2] The gas phase reaction has received relatively little attention. It would be expected, by comparison of this system with other systems and a study of the literature on the liquid phase reaction, that a rather large quantum efficiency would be obtained and that complications would arise due to the large number of products which might be formed.

## I. Experimental

The chlorine used in these experiments was a commercial product. It was introduced into the apparatus through a tube containing phosphorus pentoxide and was then purified by distillation with liquid air. During the fractionation only the middle third was retained for use.

The benzene was thiophene free and was purified by drying with phosphorus pentoxide and by distillation at low pressure.

Some early experiments were carried out with a dynamic system. The chlorine (or benzene) passed through a quartz cell exposed to the full radiation from an iron arc. The chlorine (or benzene) then joined the benzene (or chlorine) at a junction situated immediately at the exit of the cell. No stopcocks or wax joints were present in the apparatus. The interpretation of these experiments was rendered very uncertain due to the possibility of back diffusion of the substance which should not have been exposed to the radiation. The results obtained may be summarized as follows. (1) When the benzene was illuminated and then passed into the chlorine no reaction could be detected which could not, with plausibility, be ascribed to diffusion of chlorine into the illuminated zone. Reaction was detected by determining the gas uncondensed by liquid air, since hydrogen chloride has sufficient vapor pressure at liquid air temperatures to be easily detectable.[3] Illumination of the benzene alone without any chlorine present in the system gave no indication of the formation of uncondensable gas. (2) Illumination of the chlorine with subsequent passage into benzene invariably showed the formation of large amounts of uncondensable gas, presumably hydrogen chloride. In this case, also,

[1] This paper contains preliminary results obtained with the object of determining the general course of the photochemical reaction between chlorine gas and benzene vapor. Results obtained later at Brown University and bearing more specifically on the mechanism of the reaction will be published at a future date by H. P. Smith and the senior author.

[2] For a summary see Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., New York, 1928, p. 118.

[3] Calculated from the formula of Giauque and Wiebe, THIS JOURNAL, 50, 105 (1928).

there may have been slight diffusion of the benzene into the illuminated zone, although the chlorine atoms produced by the action of radiation should persist for an appreciable distance in the stream of gas. The difficulties in this type of experimentation and the uncertainties in the interpretation of the results led to its abandonment in favor of a static method.

The chlorine and benzene were prepared in the same manner in this type of experiment. The extent of the reaction was determined: (1) by change in pressure (a glass pressure gage similar to that described by Daniels[4] was employed for this purpose); (2) by determination of the amount of chlorine disappearing during the course of the reaction; (3) in some instances by micro-analysis of the solid products formed during the reaction.

Figure 1 shows a diagram of the apparatus used. The pressure gage was attached at G. $C_1$ was filled with benzene vapor previously purified. Chlorine was admitted at F and the line sealed off at this point. Liquid air was placed around the trap H and the chlorine completely condensed. The tip T was broken by the magnetic device shown just as the liquid air was removed from the trap H. The incoming benzene vapor diffused through the system including the two flasks $C_1$ and $C_2$ and the chlorine as it vaporized from H mixed with the benzene vapor and gave a uniform mixture throughout the system with the possible exception of the tubing between $C_1$ and $C_2$ which would be filled initially with a relatively large amount of chlorine. The volume of the tubing was small compared to the volume of the system as a whole.

L was a 1000-watt tungsten filament lamp. Running water flowed continuously through the two cells W and the cells E, two inches in thickness, were filled with $M/20$ potassium dichromate solution. The absorption cells were made of ordinary plate glass. The spectral region used in this investigation extended, therefore, between the approximate limits of 4500 and 6000 Å. Due to the fact that absorption by the chlorine is relatively feeble for wave lengths greater than 5000 Å., the practical limits are from about 4500 to 5000 Å.

When it was desired to determine the amount of chlorine remaining at the end of the reaction, rubber tubing leading from a nitrogen tank was slipped over the tip at F and the tip broken inside the rubber tubing. Nitrogen was admitted to the line to atmospheric pressure. Tubing was placed over A and the line flushed with nitrogen, the emerging gases being passed into a potassium iodide solution. The iodine liberated was titrated with sodium thiosulfate solution.

When it was desired to analyze the solid products deposited on the walls of $C_1$ and $C_2$, the flasks were removed from the line and washed out with ether. The crystals were dried in a vacuum desiccator. The microanalyses were not entirely satisfactory due to the small amount of material, the difficulty in obtaining completely dry crystals and to the possibility that in some cases the crystals consisted of mixtures of several compounds. The analyses aid somewhat in the final interpretation of the results. Chlorine was determined in some cases by a Carius analysis. In one run the carbon and hydrogen were determined by true microanalysis and the chlorine was obtained by difference.[5]

## II. Results and Discussion of Results

Several facts must be kept in mind in considering the results obtained. (1) Only the chlorine absorbs radiation. A detailed discussion of the band spectrum of chlorine need not be given at the present time, but

[4] Daniels, THIS JOURNAL, 50, 1115 (1928).

[5] The authors wish to express their appreciation to Dr. Irving Muskat and Dr. Kenneth Adams for performing the micro-analyses.

according to the ideas of Franck[6] and the analysis of the chlorine band spectrum as carried out by Kuhn,[7] chlorine atoms should be produced in the spectral region used. (2) Moderate pressures of chlorine and benzene were used and appreciable reaction could not be produced before the products would condense on the walls of the vessel. Phenyl chloride and *m*-dichlorobenzene are liquids with appreciable vapor pressures,[8] but most of the other possible products would have relatively low vapor pressures. With the intensities of radiation employed and the pressures used, no single step of the reaction may proceed to completion before other steps have started. (3) If the reaction is entirely one of substitution, no pressure change would be observed until products of the reaction begin to condense on the walls. With addition an immediate decrease in pressure should be observed.

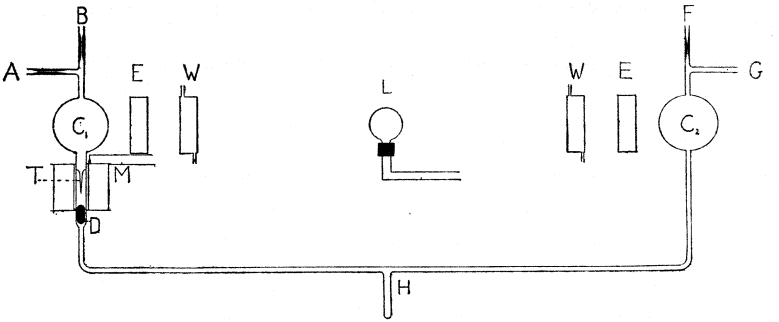


Fig. 1.

The general phenomena observed during the course of a run may be summarized as follows. (1) With very high radiation intensities, such as would be obtained by removing the dichromate filter (Fig. 1), a cloud of fine droplets would be produced almost immediately. These droplets must consist of either phenyl chloride or one of the dichlorobenzenes or perhaps a mixture of several compounds. All of the evidence points to the fact that they consist of phenyl chloride. (2) The droplets diffuse to the walls and collect there. Solid products are formed eventually on the walls. The solids seem to be produced only in and to grow out from the drops of liquid. (3) Solid is formed in the drops only in the illuminated zone. (4) In the dark no decrease in pressure could be noticed. (5) Experiments carried out with phenyl chloride in place of benzene showed solid products to be formed, at least with any rapidity, only if the phenyl chloride were admitted in such a way that it condensed on the walls.

[6] Franck, *Z. physik. Chem.*, **120**, 144 (1926); *Trans. Faraday Soc.*, **21**, 536 (1925).

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

[8] For the vapor pressure of phenyl chloride see "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, p. 220.

(a) **The Dependence of Rate of Pressure Change on the Concentrations of the Reacting Substances.**—The reactions which may occur would follow one of the two general equations

$$x\,Cl_2 + C_6H_6 = C_6H_{6-x}Cl_x + x\,HCl \text{ (Substitution)} \quad (1)$$

$$y\,Cl_2 + C_6H_6 = C_6H_6Cl_{2y} \text{ (Addition)} \quad (2)$$

In the liquid reaction the final product seems to be largely benzene hexachloride ($C_6H_6Cl_6$).[9] This compound could scarcely form in one step during a homogeneous gas phase reaction. Since phenyl chloride is formed, at least part of the reaction must proceed according to equation (1). No pressure change would be observed unless the phenyl chloride condensed on the walls.

It is of interest to ascertain the dependence of rate of pressure decrease on the pressures of the reactants. Let $p_1$ be the initial pressure of chlorine, $p_2$ the initial pressure of benzene, $p_3$ the vapor pressure of phenyl chloride, $p_4$ the pressure of chlorine and $p_5$ the pressure of benzene just at the point when the reaction system becomes saturated with phenyl chloride. Then

$$p_4 = p_1 - p_3 = p_1 - p_2 + p_5 \quad (3)$$

If $P_1$ and $P_2$ represent the total pressures at the beginning and at the instant phenyl chloride begins to condense, we may write

$$P_1 - P_2 = 0 = p_1 + p_2 - 2p_3 - p_4 - p_5 \quad (4)$$

Let $P_3$ be the total pressure at any time subsequent to the attainment of saturation with phenyl chloride and $p_6$ and $p_7$ the partial pressures of chlorine and of benzene, respectively, at that time. Then we may put

$$P_3 = p_3 + p_6 + p_7 + (p_1 - p_6) \quad (5)$$

where $(p_1 - p_6)$ is equal to the partial pressure of hydrogen chloride But

$$p_7 = p_2 - p_1 + p_6 \quad (6)$$

and

$$P_3 = p_3 + p_2 + p_6 \quad (7)$$

or

$$p_6 = P_3 - p_3 - p_2 \quad (8)$$

If the reaction is first order with respect to chlorine we would find the equation

$$k = (2.303/(t_2 - t_1)) \log (P_1 - p_3 - p_2)/(P_3 - p_3 - p_2) \quad (9)$$

to hold for all points after the system had become saturated with phenyl chloride. Up to that point the equation

$$k = (2.303/t_1) \log (P_1 - p_2)/(P_1 - p_3 - p_2) \quad (10)$$

should be valid. $t_1$ is the time required to produce saturation with phenyl chloride.

If addition takes place as well as substitution, the chlorine pressures could be calculated only if the ratio of the rates of the two reactions were

[9] Slator, *Z. physik. Chem.*, **45**, 540 (1903).

known. In this case one molecule of chlorine would disappear without hydrogen chloride formation. Thus, the decrease in total pressure would be equal to twice the decrease in partial pressure of the chlorine, *unless* some substance with low vapor pressure were chlorinated to give another substance with low vapor pressure. In that event equations of the type of equation (9) should be applicable.

In equations (9) and (10) it is possible to use $P_1$ and $P_3$ as obtained directly during a run. $p_3$ may be obtained from tables[8] and $p_2$ may be calculated from the data. Table I shows the applicability of equations (9) and (10) to the data for one run.

TABLE I

REACTION RATE AS FUNCTION OF CHLORINE PRESSURE

$P_1 = 11.70$ cm. $p_1 = 7.70$ cm. $p_2 = 4.00$ cm. $T = 25°$. (With dichromate filter)

| Time, min. | Total pressure, cm. | Chlorine pressure Eq. (8), cm. | $k$ Eqs. (9) and (10) |
|---|---|---|---|
| 0 | 11.70 | (7.70) | |
| 780 | 11.36 | 6.24 | $2.4 \times 10^{-4}$ |
| 2220 | 10.26 | 4.80 | 1.9 |
| 3660 | 9.47 | 3.85 | 1.5 |
| 5100 | 8.33 | 2.87 | 2.0 |
| 7170 | 7.42 | 1.88 | 2.0 |
| 8610 | 6.91 | 1.33 | 2.5 |
| | | | Av. 2.0 |

One additional run made with somewhat lower benzene pressure and nearly three times the initial chlorine pressure showed an average constant of $2.2 \times 10^{-4}$ until the pressure changes became too small to be measured with accuracy.

Table II shows data for a run made without the dichromate filter. In this case solid was deposited in less than ten minutes and condensation of phenyl chloride took place even before the first pressure reading could be taken. Under these conditions the pressure of the chlorine should be equal approximately to its initial pressure minus the change in total pressure. This statement should be especially applicable after the early stages of a run. The constants are calculated on this basis. The pressure changed for some time after the last reading given in the table, but this simple type of calculation is not applicable when the change in total pressure is too large, for the benzene is being converted into substances of very low vapor pressure by addition as well as by substitution. Strictly speaking this method of calculation is valid only when a substance of low vapor pressure is being chlorinated to give another substance of low (or at least the same) vapor pressure. The data in Table II indicate that this condition is fulfilled approximately for a time after the early stages of the run, but negative chlorine pressures would be found toward the end if this calculation were carried to the limit.

TABLE II

REACTION RATE AS FUNCTION OF CHLORINE PRESSURE

$P_1 = 11.10$ cm. $p_1 = 7.25$ cm. $p_2 = 3.85$ cm. $T = 25°$. (Without dichromate filter)

| Time, min. | Total pressure, cm. | Pressure chlorine (calcd.), cm. | $k$ |
|---|---|---|---|
| 0 | 11.10 | (7.25) | |
| 10 | 10.03 | 6.18 | $1.6 \times 10^{-2}$ |
| 18 | 7.50 | 3.65 | 7.2 |
| 25 | 6.05 | 2.20 | 6.2 |
| 35 | 5.04 | 1.19 | 8.3 |
| 45 | 4.37 | 0.52 | 6.6 |
| | | | Av. 7.1 (last four) |

One other run with a slightly higher chlorine pressure gave constants for a short time averaging about $7.7 \times 10^{-2}$.

Thus we see that with moderate benzene pressures the rate of reaction is, to a first approximation, proportional to the chlorine pressure. The spectral region is such that absorption of the radiation is far from complete, so that the rate is probably proportional to the intensity of the radiation absorbed rather than to the chlorine pressure as such.

The initial benzene pressures did not vary greatly from one run to another (See Table IV), but no direct connection could be found between pressure of benzene and rate under the conditions of these experiments. This means, presumably, that reaction takes place appreciably on the walls, at least after the initial stages of a run. Further investigation of this point will be made later.

(b) **The Analysis by Titration of Chlorine Disappearing** —An independent check on the value of the reaction rate constant may be obtained from analytical data. Referring to the run given in Table I, the number of moles of chlorine calculated from the initial pressure is 0.00884. At the end 51.38 cc. of 0.1130 sodium thiosulfate was required to react with the iodine liberated by the chlorine. There was, therefore, 0.00290 mole of chlorine left at the end of the run. The total time of exposure was 8630 minutes. Therefore, $k = 2.303/8630 \log (884/290) = 1.3 \times 10^{-4}$, a fair check with the values given in the table. The average constant, for runs with the dichromate filter, calculated in this manner is $3.7 \times 10^{-4}$. Without the dichromate filter the results calculated by the two methods are less comparable (Runs 7 and 8) since these runs were continued for some time after noticeable pressure changes had stopped. The small amounts of chlorine at the end gave relatively large chances for error both in removing it from the line and in the titration.

Table III presents a summary of the results obtained from analytical data.

With the exception of the first run, in which some error seems to have been introduced, not more than four atoms of chlorine have been used per

TABLE III

NUMBER OF MOLES OF REACTANTS

| Run no. | Initial moles of benzene | Initial moles of chlorine | Final moles chlorine | Atoms Cl used/ moles benzene |
|---|---|---|---|---|
| 1 | 0.0041 | 0.0234 | 0.0061 | 8.4 |
| 2 | .0053 | .0261 | .0163 | 3.7 |
| 3 | .0058 | .00227 | .00032 | 0.7 |
| 4 | .0043 | .00161 | .00088 | 0.3 |
| 6 | .0043 | .00884 | .00290 | 2.8 |
| 7 | .0044 | .00819 | .00020 | 3.6 |
| 8 | .0044 | .00902 | .00035 | 3.9 |

initial benzene molecule. This means, probably, that a mixture of products is always formed.

(c) The Total Pressure Change during Reaction.—If the reaction is entirely one of substitution, the final pressure should be equal to the initial pressure of the chlorine, providing the vapor pressures of the organic products are negligible. If the reaction is one of addition, the final pressure should approach the vapor pressures of the products provided neither the chlorine nor the benzene is in too great excess. Table IV summarizes the data on initial and final pressures.

TABLE IV

TOTAL CHANGE IN PRESSURE

| Run no. | Initial pressure of chlorine, cm. | Initial pressure of benzene, cm. | Total initial pressure, cm. | Final pressure, cm. | Time, hrs. | Conditions |
|---|---|---|---|---|---|---|
| 1 | 20.7 | 3.6 | 24.3 | 19.1 | 43 | Dichromate filter |
| 2 | 22.9 | 4.6 | 27.5 | 22.1 | 8 | |
| 3 | 2.0 | 5.1 | 7.1 | 4.8 | 48 | |
| 4 | 1.4 | 3.7 | 5.1 | 2.3 | 48 | |
| 6 | 7.9 | 3.8 | 11.7 | 6.9 | 143 | |
| 7 | 7.2 | 3.9 | 11.1 | 2.4 | 14 | No filter |
| 8 | 7.8 | 3.7 | 11.5 | 1.5 | 17 | |

It is obvious that substitution will not account for the entire pressure change in some of the runs.

(d) Characteristics of the Solid Products Formed.—Carius analyses of the chlorine content of the solid products were carried out for Runs 1 and 2. Carbon and hydrogen analyses were made for Run 6.[5]

For Run 1 the percentage of chlorine in the solid removed from the walls was 58.18. For Run 2 it was 57.95. The only known compound having a composition near this figure is trichlorobenzene ($C_6H_3Cl_3$) with a theoretical percentage of 58.63. The hypothetical compound $C_6H_5Cl_3$ would contain 57.99% of chlorine.

For Run 6, which lasted 143 hours, the following results were obtained

| | Found | | | Theoretical ($C_6H_6Cl_6$) |
|---|---|---|---|---|
| Percentage H | 2.29 | 1.99 | Av. 2.14 | 2.08 |
| Percentage C | 24.69 | 25.65 | 25.17 | 24.76 |
| Percentage Cl (by difference) | 73.02 | 72.36 | 72.69 | 73.16 |

Melting points were determined for some of the products. In no case were very sharp melting points obtained. In one run (not shown above) the solid melted from 118 to 122°. γ-Benzene hexachloride melts at 112° and the δ-form at 129°. The α- and β-forms melt at widely removed temperatures. The solid obtained in Runs 1 and 2 did not have a sharp melting point, but melted from approximately 50 to 105°.

(e) **Conclusions.**—The rate of removal of chlorine from the gas phase in the chlorination of benzene under the conditions of these experiments is proportional to the pressure of the chlorine. This means, probably, that the rate is proportional to the intensity of the radiation absorbed and that the production of atoms is sufficient to initiate the reaction. The reaction, at least in the early stages, is unquestionably a chain reaction. Such chains are possible theoretically and facts concerning the mechanism will be brought out at a later date. It is interesting to note, however, that Luther and Goldberg[10] found the rate of photochemical chlorination of liquid benzene to be proportional to the pressure of the chlorine and that Bodenstein[11] estimated the quantum efficiency to be as high as $10^6$.

One of the products is unquestionably phenyl chloride and the chain mechanism leads also logically to the formation of hydrogen chloride. The phenyl chloride is soon adsorbed on the walls and before reaction has proceeded very far begins to condense. Later stages probably involve several simultaneous reactions. Slator[9] found benzene hexachloride, $C_6H_6Cl_6$, as one of the main products in the liquid reaction. Meidinger[12] found phenyl bromide and benzene hexabromide in the bromination of benzene. Benzene hexachloride is formed unquestionably as one of the final products in the present experiments. Addition of chlorine to benzene must be taking place, therefore, as well as substitution. The isolation of definite intermediate compounds would be difficult if not impossible. It would seem unreasonable for the addition of chlorine to benzene to be a homogeneous gas phase photochemical reaction and what evidence is presented in this article is distinctly against such an assumption. The addition of a chlorine atom to a benzene molecule could probably take place only as the result of a triple collision and the resulting unsaturated molecule formed would have to acquire another chlorine atom either from some chlorine molecule or by absorbing a free atom produced photochemically. The former step seems improbable and the latter mechanism would involve a peculiar power of the light intensity in the rate equation.

[10] Luther and Goldberg, *Z. physik. Chem.*, **56**, 43 (1906).

[11] Bodenstein, *ibid.*, **85**, 329 (1913).

[12] Meidinger, *ibid.*, **5B**, 29 (1929).

We may offer the following tentative description of the phenomena taking place. (1) A chain reaction is first produced leading to the formation of phenyl chloride and hydrogen chloride. (2) The phenyl chloride condenses on the walls. (3) Several things may now happen. By analogy with the addition of chlorine to phenyl iodide,[13] the compound $C_6H_5Cl_3$ may be formed. While analyses of solids from two different runs give the proper halogen content, too great weight should not be given to this evidence due to the possibility of a mixture being present. This hypothetical compound would probably not be formed by the addition of a chlorine molecule to the ring of phenyl chloride, but would be a molecular compound of some type. It might split out hydrogen chloride and give one of the dichlorobenzenes upon heating. It might, however, act as a good chlorinating agent and play a part in the addition of chlorine to the benzene which would dissolve unquestionably in the phenyl chloride. The fact that crystals are first produced in the liquid drops on the walls in the illuminated zone indicates that the addition reaction takes place in the liquid phase and not as a homogeneous gas phase reaction. The extent of the addition should vary with time, but in agreement with previous work the final product seems to be benzene hexachloride. The results point distinctly to the fact that addition is of primary importance once sufficient phenyl chloride is produced to give a layer on the walls.

Results obtained at sufficiently low pressure to keep the phenyl chloride from condensing will be presented at a later date.

## Summary

1. The photochemical chlorination of benzene at moderate pressures has been studied. The rate of reaction is approximately proportional to the chlorine pressure.

2. The first step leads to the production of phenyl chloride, but this substance condenses on the walls and a liquid reaction ensues which involves largely addition, probably to benzene dissolved in the phenyl chloride, the final product being mostly benzene hexachloride.

MEMPHIS, TENNESSEE, AND PROVIDENCE, RHODE ISLAND

[13] Willgerodt, *Chem. Centr.*, **16**, 833 (1885).

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

# TRIATOMIC HALOGEN MOLECULES IN PHOTOCHEMICAL REACTIONS

BY G. K. ROLLEFSON AND HENRY EYRING

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In recent years it has become generally accepted that the primary action of the light in photochemical reactions involving the halogens is a dissociation of the molecule into two atoms.[1] In building up mechanisms for such reactions the possibility of the existence of $X_3$ molecules has been raised; as for example, Göhring[2] in discussing the reaction between $H_2$ and $Cl_2$ introduced $Cl_3$ as an intermediate and Lenher and Rollefson[3] assumed what amounts to that in postulating a specific action of $Cl_2$ in the formation of COCl as an intermediate in the phosgene synthesis. Recent developments in quantum mechanics have made it possible to investigate the stability of $X_3$ molecules from theoretical considerations.[4] While there may be some question concerning the exactness of such calculations, nevertheless we feel that limiting values and probable values which are of significance can be obtained.

In this paper we shall apply these methods to the halogens and discuss the significance of the results in a few special cases.

Three monovalent atoms form the most stable configuration when they are in a straight line. For three atoms in a straight line the formula for the binding energy

$$E_3 = A + B + C + \sqrt{\frac{1}{2}((\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2)} \qquad (1)$$

may be expected to apply for $p$ electrons.

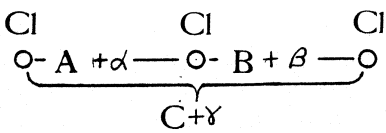


Fig. 1.

Figure 1 represents three chlorine atoms. The energy written between pairs is that which would be required to separate them if the other atom were absent. The quantities, $A + \alpha$, $B + \beta$, $C + \gamma$, can be determined from the Morse curve for chlorine and will depend only on the distance between the atoms.[5]

The Morse curve is

$$E_2 = D(2e^{-a(r-r_0)} - e^{-2a(r-r_0)}) \qquad (2)$$

[1] This occurs directly if the absorption is in the continuum and probably occurs as a second step if the band absorption is used.

[2] Göhring, *Z. Elektrochem.*, **27**, 511 (1921).

[3] Lenher and Rollefson, THIS JOURNAL, **52**, 500 (1930).

[4] Eyring and Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

[5] Morse, *Phys. Rev.*, **34**, 57 (1929).

$A + \alpha$, $B + \beta$, $C + \gamma$ are functions of $r$, the distance in Ångströms between the chlorine atoms, and are the values $E_2$ takes for the corresponding distances. $D'$ is the heat of dissociation, $D$, of the molecule plus a half quantum of vibrational energy; $r_0$ is the distance between the atoms corresponding to the lowest potential energy; $a$ is determined by the equation

$$a = 0.1227\, W_0(M/D') \qquad (3)$$

$W_0$ is the vibration frequency of the molecule in its lowest quantum state expressed in wave numbers. $D'$ has been defined and must be expressed in wave numbers. $M$, the reduced mass, is defined by the equation $M = M_1M_2/(M_1 + M_2)$ where $M$ and $M_2$ are the two atomic weights.

TABLE I

CONSTANTS USED IN CONSTRUCTING THE MORSE CURVES

| Gas | $D$ | $D'$ | $r_0$ | $a$ | $W_0$ |
|---|---|---|---|---|---|
| $F_2$ | 72 | 73.5 | 1.4 | 2.52 | 1071.5 |
| $Cl_2$ | 58 | 58.8 | 1.74 | 2.22 | 570 |
| $Br_2$ | 45.7 | 46.2 | 2.26 | 2.00 | 326.6 |
| $I_2$ | 34.5 | 34.8 | 2.66 | 1.50 | 213.9 |

To determine $E_3$ it is necessary to know the ratio of the coulombic binding, $A$, $B$, $C$, to the corresponding interchange binding $\alpha$, $\beta$ and $\gamma$.

Curves are drawn for chlorine with $E_3$ as ordinate and the distance between the central chlorine atom and an outside one as abscissa, keeping the distance between the central Cl atom and the other outside atom equal to $1.74 \times 10^{-8}$ Å., the normal distance for $Cl_2$.

If the calculations are carried out for all possible separations of the atoms, it is found that the real energy minimum occurs for a configuration in which the chlorine molecule has expanded 0.02 Å. and the minimum is 0.1 k. cal. deeper than we have plotted it. This expansion is negligible, however, and is ignored throughout.

For Curve 1 in Fig. 2 it is assumed that $A = B = C = 0$; *i. e.*, that the entire binding is valence or interchange binding. For Curve 2 it is assumed that

$$\frac{\alpha}{A + \alpha} = \frac{\beta}{B + \beta} = \frac{\gamma}{C + \gamma} = 90\%$$

for all distances, $r$, used in the calculation. This is the theoretical value of the ratio for $H_2$. For Curve 3 it is assumed that $\alpha = \beta = \gamma = 0$, *i. e.*, that there is no valence binding, the whole being the so-called coulombic binding. The actual curve must lie between 1 and 3.

Curves similar to 1, 2 and 3 of Fig. 2 were drawn for $F_2$, $Br_2$ and $I_2$. They are just the same in their general form as those given here for $Cl_2$.

In Table II, Curves 1, 2 and 3 have the same meaning as in Fig. 2. $r$ of the last column refers to the distance between the approaching atom and the near atom of the diatomic molecule at which the potential energy is a

TABLE II

VALUES OF THE ACTIVATION ENERGIES FOR THE FOUR GASES

| Gas | Curve | Activation energies $x_3 + x = x_3$ | Activation energies $x_3 = x_2 + x$ | $\Delta H$ $x_3 + x = x_3$ | $r$ Ångströms, maximum |
|---|---|---|---|---|---|
| | 1 | 12.2 | 8.2 | + 4.0 | 1.87 |
| $F_2$ | 2 | 6.2 | 10.2 | − 4.0 | 1.95 |
| | 3 | 0 | 77.7 | −77.7 | .. |
| | 1 | 8.6 | 6.3 | + 2.3 | 2.24 |
| $Cl_2$ | 2 | 4.5 | 8.6 | − 4.1 | 2.39 |
| | 3 | 0 | 61.1 | −61.1 | .. |
| | 1 | 6.3 | 5.4 | + 0.9 | 2.88 |
| $Br_2$ | 2 | 3.5 | 7.3 | − 3.8 | 3.02 |
| | 3 | 0 | 47.3 | −47.3 | .. |
| | 1 | 5.1 | 3.8 | + 1.3 | 3.45 |
| $I_2$ | 2 | 2.6 | 5 | − 2.4 | 3.58 |
| | 3 | 0 | 36.3 | −36.3 | .. |

maximum. After this distance $r$ has been passed, the $X_3$ atom will not dissociate for a time corresponding to a great number of vibrations even though it is not stabilized by collision with another molecule.

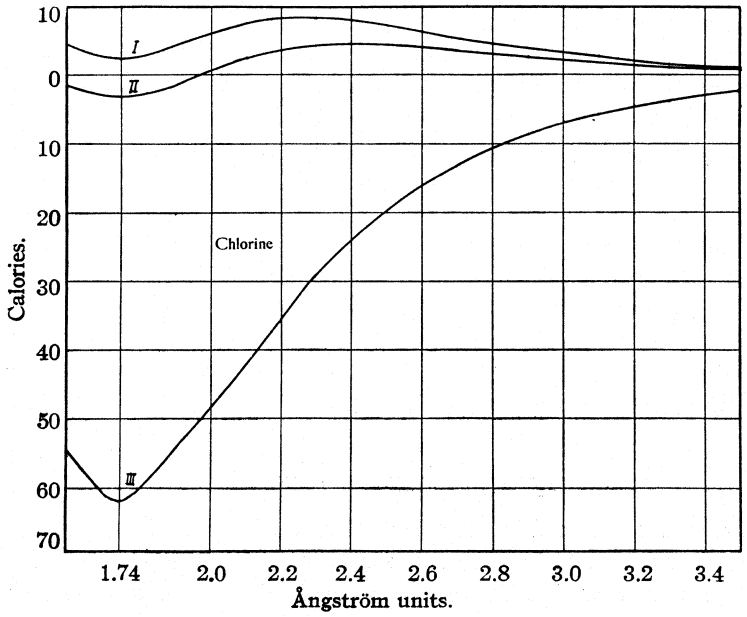


Fig. 2.

This may be seen in the following way. If the two distances between the outer atoms and the central atom of a linear $X_3$ molecule be taken as axes making an angle of 120° with each other and the corresponding energy $E_3$ of Equation 1 be plotted, a contour map is obtained. If the corresponding

energy surface is constructed, it can be shown, by the method of Wigner[4] (pp. 305–309) that a ball rolling on this surface will describe the behavior of the $X_3$ molecule. The surface consists essentially of a roughly triangular basin lying in the pass separating two valleys which make an angle of 120° with each other. The formation of an $X_3$ molecule corresponds to a ball rolling up one valley passing over a pass into the basin. The ball will not find its way through the other pass into the adjoining valley on the first trial. For such a triangular basin this will require many trials. In fact, the ball may after repeated trials return over the pass by which it entered. In any case the quasimolecule will have a very long life as compared with the duration of an ordinary collision. The gentle slopes contribute to the long life by making the individual vibrations slow.[6]

Another point which this surface reveals is that all the activation energy is translational. This is apparent because the gap into the basin is almost exactly along the axis of the valley and the ball will require only longitudinal motion along the valley (translational energy) to pass into the basin. Transverse motion which represents vibration of the $X_2$ molecule is not helpful. The fact that the gap lies along the axis of the valley corresponds to the fact that the activation energy is for a configuration in which there is no expansion of the original $X_2$ molecule due to the presence of the third atom.

The negative values of $\Delta H$ for the reaction $X_2 + X = X_3$ in Table II point to the stability of $X_3$ at low temperatures. The equilibrium for this reaction may be calculated if we have a value for the entropy change. This entropy change must lie between zero and the value for $X = {}^1/_2X_2$ which is about minus ten. A reasonable estimate, which we shall use, is minus six. This gives for the equilibrium constant $K_p$

$$K_p = \frac{(X_3)}{(X)\,(X_2)} = e^{-\Delta H/RT}\, e^{\Delta S/R} = 0.05e^{-\Delta H/RT}$$

To apply this to a particular case consider the data for iodine for which the dissociation $I_2 = 2I$ has been investigated by Starck and Bodenstein[7] on the assumption that there is no $I_3$. Using the value of $\Delta H$ given in Table II for $I + I_2 = I_3$, according to Curve 2

$$K_p = \frac{(I_3)}{(I)\,(I_2)} = 0.05e^{2400/2\times T}$$

For

$T = 300$ $K_p = 2.75$ $T = 1200$ $K_p = 0.14$

This shows that at room temperature the principal molecule, other than $I_2$, is $I_3$ but at high temperatures it is I. The amount of $I_3$ calculated for 1200°A.

[6] An example of a triatomic quasimolecule of long life has been pointed out recently by Volmer, [*Z. physik. Chem.*, **13B**, 299 (1931)].

[7] Starck and Bodenstein, *Z. Elektrochem.*, **16**, 965 (1910).

on the basis of the data given above is large enough so that it might have been detected in the experiments of Starck and Bodenstein but not with any great certainty. The absolute values obtained by these calculations are, however, too sensitive to slight changes in $\Delta H$ or $\Delta S$ to be considered very accurate. For the other halogens where the $\Delta H$ is larger and the $\Delta S$ is practically the same, the percentage in the form of $X_3$ would be considerably greater.

From what has been said it follows that all reactions such as photochemical reactions at room temperature, in which a dissociation of the chlorine molecule has been postulated as a primary step, should be considered as involving $Cl_3$ molecules. If this is the case we should expect to find chlorine atoms in the first excited state, the $^2P_{1/2}$ state, more reactive than normal atoms since they possess some of the activation energy necessary to form $Cl_3$. Whether all of the difference in energy between the $^2P_{1/2}$ and the $^2P_{3/2}$ states of the atom can be considered as available for a process of this kind cannot be stated definitely but it is possible to say that at least a considerable portion is available. For example, let us consider that the excited chlorine atom collides with some molecule and the excitation energy is converted into translational energy; the division of the energy between the two colliding molecules will depend upon their masses. For a collision between a chlorine atom and a chlorine molecule, the atom will acquire two-thirds of the energy. Lacking more definite information, let us assume that the total energy difference, $^2P_{3/2} - {}^2P_{1/2}$, amounting to 2.5 k. cal. for Cl atoms is available as activation energy for the reaction to form $Cl_3$. Then we should expect the excited atoms to react $e^{2500/600} = 65$ times as often as the normal atoms. This is quite in accord with the experiments of Rollefson and Lindquist[8] in which they demonstrated that the excited atoms would cause the formation of hydrochloric acid at an easily measurable rate, whereas the normal atoms produced no effect under the same conditions. In those experiments the situation was somewhat more complicated in that the chlorine atoms had a chance to react with ICl before acquiring sufficient energy to form $Cl_3$. This resulted in the observed difference in rates being greater than the factor given above. These arguments would hold for any other mechanism in which an activation energy was required for the chlorine atom to react. The difference would disappear if the following reactions were so slow that $Cl_3$ was at its equilibrium concentration.

The next stage in the photosynthesis of hydrochloric acid by visible light must involve water. In a previous paper[9] one of us has postulated that the chlorine atom forms an addition compound with water which is capable of reacting with hydrogen. This possibility has been discussed

[8] Rollefson and Lindquist, THIS JOURNAL, 52, 2793 (1930).

[9] Rollefson, *ibid.*, 51, 770 (1929).

also by Franck and Rabinowitsch[10] and by Bodenstein.[11] In the latter paper it is argued that the $ClH_2O$ molecule is formed so slowly that its only function must be to start rather long chains yielding HCl. Let us examine these arguments in detail.

Coehn and Jung found that in a particular experiment in which the concentration of water vapor was $10^{-9}$ mole/liter, the rate of formation of HCl was $3 \times 10^{-5}$ mole/sec. If half of this was due to reaction of $ClH_2O$ with hydrogen, then $k'(ClH_2O)(H_2) = 10^{-5}$ mole/sec. Now it would be necessary for $ClH_2O$ to be formed with this same speed so we could say that $k(Cl)(H_2O) = 10^{-5}$ mole/sec., in which case Bodenstein says that the maximum value of $k$ is $10^{11}$, the collision number for a bimolecular reaction, neglecting the fact that a three-body collision is needed to stabilize the molecule formed. From the standpoint of the results we have presented the equation should be written $k_1(Cl_3)(H_2O) = 10^{-5}$ mole/sec., in which case $10^{11}$ instead of being considered the maximum value of $k_1$ must be considered as a reasonable value. Using unpublished data Bodenstein takes $10^{-10}$ as the concentration of chlorine atoms; this seems like a reasonable value, so we shall use the same for the concentration of $Cl_3$. This gives $k_1(Cl_3)(H_2O) = 10^{-8}$ mole/sec., a value a thousand-fold too small for the $ClH_2O$ molecule to be involved in the formation of half the HCl. That would mean that the chains started by $ClH_2O$ would have to result in the formation of 1000 moles of HCl. Bodenstein's suggestion for this is that the hydrogen atom formed in the reaction

$$ClH_2O + H_2 = HCl + H_2O + H$$

catalyzes the reaction between hydrogen and chlorine molecules. Regardless of what mechanism is postulated for such a catalysis, we can say that the quantum yield obtained in the study of the reaction with very dry gases indicates that the yield must be very much less than 1000 molecules of HCl for each hydrogen atom produced. Coehn and Heymer[12] give the quantum yield of the dry reaction as less than seven; if we are more liberal we can say that as many as ten molecules may be formed but that still leaves the rate of formation of $ClH_2O$ too small by a factor of one hundred. Probably at least a factor of ten in this could be put onto uncertainties in the water and $Cl_3$ concentrations, the remaining factor of ten must be attributed to larger collisional diameters or other factors which might increase $k_1$.[13]

[10] Franck and Rabinowitsch, *Z. Elektrochem.*, **36**, 794 (1930).

[11] Bodenstein, paper presented at the meeting of the Faraday Society, April 16–17, 1931.

[12] Coehn and Heymer, *Naturwissenschaften*, **14**, 299 (1926).

[13] A recent paper by Schumacher and Stieger, [*Z. physik. Chem.*, **B13**, 169–189 (1931)] on the chlorine sensitized photosynthesis of carbon dioxide reports chlorine atom concentrations of 2 to $6 \times 10^{-9}$ mole/liter. If we use these values instead of the $10^{-10}$ reported by Bodenstein the desired rates are obtained without difficulty.

We would suggest the following mechanism for the reaction between hydrogen and chlorine

$$(1)\quad Cl_2 + h\nu = Cl + Cl^*$$
$$(2)\quad Cl^* + Cl_2 = Cl_3$$
$$(3)\quad Cl_3 + H_2O = ClH_2O + Cl_2$$
$$(4)\quad ClH_2O + H_2 = HCl + H + H_2O$$
$$(5)\quad H + Cl_2 = HCl + Cl$$

The reaction of H with $Cl_2$ is exothermic to the extent of approximately 45 k. cal. If we consider this amount as divided approximately equally between the products, the chlorine atom will have kinetic energy equivalent to 22.5 k. cal. According to calculations by Eyring,[14] this is greater than the probable activation energy necessary for the atom to react with $H_2$ without the intervention of water. Therefore we would say that the chain proceeded by (5) and

$$(6)\quad Cl + H_2 = HCl + H$$

until the atoms are removed by some other reaction. Or a chlorine atom loses so much of its energy by ineffective collisions that it is no longer able to react with hydrogen. According to these views the reaction with dry gases is brought about by light of such frequencies that the Cl atoms produced have enough energy to react with hydrogen. Such being the case, the measurements of Coehn and Heymer give the length of the chains due to (5) and (6) as being of the order of magnitude of ten. This gives the same mechanism to the union of the dry and the moist gases except that in the dry gases there is no way to continue the chain if the kinetic energy of the chlorine atom drops below a critical value, whereas in the moist gases the chain may be continued through the formation of $ClH_2O$.

Another reaction of interest is the photochemical formation of phosgene. A mechanism for this reaction has been proposed by Lenher and Rollefson[3] which involves the formation of an intermediate molecule COCl according to the equation

$$CO + Cl + Cl_2 = COCl + Cl_2$$

Opponents of this mechanism have objected to this step on the ground that it involved a more specific effect on the part of the chlorine molecule than had been found in any other reaction. In the light of the results which have been presented in this paper we see that the above equation should be replaced by

$$CO + Cl_3 = COCl + Cl_2$$

which is equivalent to saying that the chlorine molecule has an effect which could be duplicated only by molecules capable of forming loose addition products with chlorine atoms. Therefore it is not surprising that this effect has not been found with other molecules. The calculations of this

[14] Eyring, THIS JOURNAL, 53, 2537 (1931).

paper must be considered as giving a very definite justification for the assumption of a very specific action of chlorine molecules in reactions of the type written above.

Next let us consider what explanation may be offered for the results of Senftleben and Germer,[15] who carried out experiments to demonstrate the dissociation of the halogens by light. Their experiments consisted of illuminating the halogens in a Pirani gage and measuring the change in heat conductivity of the gas. Due to disturbing factors no quantitative data were given but if we assume that the apparatus used had the same sensitivity as that used by Senftleben and Riechemeier[16] in their work on atomic hydrogen, then we can say that the concentration of halogen atoms necessary to give a pronounced effect would be of the order of $10^{-7}$ or $10^{-8}$ mole/liter. This is a much higher value than that given by Bodenstein and must be considered as too high to be compatible with the results from photochemical reactions. According to the views we have expressed, the principal product formed by the light in the experiments of Senftleben and Germer would be $X_3$ and not halogen atoms; therefore, the increased loss in heat from the hot wire of the Pirani gage could not be attributed to an increase in heat conductivity of the gas due to a decrease in the average molecular weight. The observed effect can be explained as due to dissociation of the $X_3$ molecules at the hot wire, thus causing more heat to be taken from the wire than would be the case if only $X_2$ molecules were present.

## Summary

By using the quantum mechanics equation for the potential energy of systems of three atoms, it has been shown that for all the halogens the molecules of the type $X_3$ are stable at room temperature with respect to the decomposition into $X_2$ and X. The significance of this fact has been discussed in connection with the mechanism for the reactions between chlorine and hydrogen and between chlorine and carbon monoxide. For the hydrogen–chlorine reaction it has been shown that the mechanism of the reaction is essentially the same for dry gases as for moist. The results of Senftleben and Germer on the optical dissociation of the halogens have been interpreted from the standpoint of the conclusions presented in this paper.

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[15] Senftleben and Germer, *Ann. Physik*, [5] **2**, 847 (1929).

[16] Senftleben and Riechemeier, *ibid.*, [5] **6**, 105 (1930).

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE UNIVERSITY OF NORTH CAROLINA]

# DETERMINATION OF ALUMINUM. FORMATION OF LITHIUM ALUMINATE

BY J. T. DOBBINS AND J. P. SANDERS

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## Introduction

The formation of lithium aluminate has been studied by D. Prociv.[1] He used the method of J. Hegrousky,[2] for preparing acid lithium aluminate. This method consists of dissolving strips of amalgamated aluminum in normal and tenth normal solutions of lithium hydroxide. He states also that lithium aluminate is precipitated by the addition of a solution of lithium hydroxide to a solution of aluminum salts, or by adding a solution of lithium salt to a solution of alkaline aluminate. In all cases the composition of the compound was expressed by the formula $LiH(AlO_2)_2 \cdot 5H_2O$, which upon moderate ignition was transformed into $Li_2O \cdot 2Al_2O_3$. The solubility of lithium aluminate was found by Prociv to be $1.2 \times 10^{-4}$ gr. eq. per liter at 25°. This suggests a possible method of determining aluminum quantitatively by addition of an excess of lithium salt solution to the aluminum solution and making the solution alkaline.

## Reagents

**Solution of Lithium Chloride.**—A 10% solution is made by dissolving 100 g. of lithium chloride in distilled water and making the volume up to 1 liter with water, or by dissolving the required amount of lithium carbonate in a small amount of water, adding hydrochloric acid and making the volume up to 1 liter with water.

**Ammonium Hydroxide Solution.**—Approximately $N/10$ solution is used as it is easier to secure the exact alkalinity of the solution by adding the very dilute solution dropwise.

**Indicator.**—Phenolphthalein is used as indicator. The required alkalinity of the solution is a faint pink that is just perceptible.

**Standard Aluminum Nitrate Solution.**—The solution is made by dissolving 30 g. of aluminum nitrate and making up to 1000 cc. This solution is standardized by evaporating 25 cc. to dryness, igniting and weighing the resulting $Al_2O_3$.

## Procedure

Aliquot portions of the aluminum salt, sufficient to give approximately 0.1 g. of lithium aluminate, are placed in a beaker and the volume made up to 100 cc. with water. To this solution are added a few drops of phenolphthalein and lithium chloride solution in excess of that required to precipitate the estimated amount of aluminum in the sample. Dilute ammonium hydroxide is added drop by drop with stirring until a very faint pink color is detected. If too much ammonium hydroxide is added, dilute hydrochloric acid is added until the desired pink tint is obtained. A voluminous, flocculent precipitate is formed that filters very rapidly and washes easily. The precipitate is allowed to settle

[1] Prociv, *Collection des Travaux de Czechosolvak*, **1**, 95 (1929).

[2] Hegrousky, *J. Chem. Soc.*, **118**, 1013 (1920).

for five minutes, filtered and washed with distilled water until free from chlorides. An 11-cm. filter paper is required for a sample giving a precipitate weighing approximately 0.1 g. After washing is complete, the filter paper with the precipitate is transferred to a crucible and placed in a low temperature oven until dry. Then the temperature is raised and the precipitate is ignited, at a high temperature, to constant weight. The precipitate is weighed and aluminum calculated from the formula $2Li_2O_2 \cdot 5Al_2O_3$.

## Experimental Results

The results, expressed in grams of $2Li_2O \cdot 5Al_2O_3$, obtained from samples of pure aluminum nitrate solution are given in Table I.

TABLE I

EXPERIMENTAL RESULTS

| I $2Li_2O \cdot 5Al_2O_3$, g. | II $2Li_2O \cdot 5Al_2O_3$, g. | III $2Li_2O \cdot 5Al_2O_3$, g. | IV $2Li_2O \cdot 5Al_2O_3$, g. |
|---|---|---|---|
| 0.1084 | 0.1071 | 0.0996 | 0.1031 |
| .1090 | .1073 | .0994 | .1028 |
| .1084 | .1066 | .0997 | .1027 |
| .1084 | .1080 | .0998 | .1029 |
| .1082 | .1070 | .0999 | .1034 |
| Av. .1085 | Av. .1072 | Av. .0997 | Av. .10298 |
| Calcd. .1083 | Calcd. .1070 | Calcd. .0996 | Calcd. .1030 |

## Discussion of Results

Since the precipitate is very voluminous this method requires the use of a large filter paper. The precipitate comes down in a flocculent form that filters and washes very rapidly. The time required to filter and wash a series of twelve samples of lithium aluminate precipitate is not more than an hour. At the same time a large volume of water will have passed through the precipitate. These facts render this method much more desirable than the accepted method in which the aluminum is precipitated with ammonium hydroxide.

The method gives more concordant results than those obtained by the ammonium hydroxide process.

The most satisfactory results are obtained when the weight of lithium aluminate is not more than 0.1 g. A little experience will enable one to determine the size of aliquot to use in order to obtain approximately this weight. Precipitates weighing very much more than 0.1 gram are so bulky that they are unwieldy in transferring and washing.

D. Prociv suggested this as a method for the determination of lithium, but said the precipitate, after ignition, is weighed as $Li_2O \cdot 2Al_2O_3$. From his solubility determinations he concluded that the precipitate contains lithium and aluminum in the ratio of 0.8Li : 2Al, which, he says, is an atomic ratio of approximately 1Li : 2Al. In fact, this is an atomic ratio of 2Li : 5Al. This corresponds to the formula $2Li_2O \cdot 5Al_2O_3$ which was found in this investigation.

The precipitation should be made in solutions just alkaline to phenolphthalein. Ammonium hydroxide is used instead of sodium hydroxide or potassium hydroxide since it is volatile and in case some ammonium salt remains in the precipitate after washing, it will be volatilized during ignition of the precipitate.

The method has been used, with excellent results, in some alum investigations. It is applicable under any conditions in which the ammonium hydroxide method can be used.

## Summary

1. Aluminum may be determined quantitatively as lithium aluminate.
2. Lithium aluminate precipitate is filtered and washed much more rapidly than aluminum hydroxide.
3. More concordant results are obtained by this process than by the ammonium hydroxide method.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN COLLEGE OF MINING AND TECHNOLOGY]

# AN OVERLOOKED SOURCE OF ERROR IN THE FERROCYANIDE TITRATION OF ZINC

BY BARTHOLOW PARK

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The ferrocyanide method of determining zinc proposed by Fahlberg,[1] and modified by Low[2] and Demorest,[3] includes the addition of hydrogen sulfide or hydrogen sulfide water just before the titration.

Hydrogen sulfide is added to precipitate copper and to reduce any bromine, chlorine or chlorate which might be present in the zinc solution. The fact that ferricyanide is also reduced by hydrogen sulfide has apparently been overlooked.

When a solution of ferrocyanide stands, a small amount of ferricyanide is formed. According to Kolthoff,[4] this change is hastened by light. Even in freshly prepared solutions of ferrocyanide there is usually a little ferricyanide. During the zinc titration, if hydrogen sulfide is present, this ferricyanide is reduced to ferrocyanide, which reacts with the zinc. If no hydrogen sulfide is present, there is no reaction between

[1] Fahlberg, *Z. anal. Chem.*, **13**, 379 (1874).

[2] Low, "Technical Methods of Ore Analysis," 9th ed., John Wiley and Sons, Inc., New York, **1922**, p. 252.

[3] Lord and Demorest, "Metallurgical Analysis," 5th ed., McGraw-Hill Book Co., Inc., New York, **1924**, p. 203.

[4] Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, **1928**, Vol. I, p. 239.

the ferricyanide and the zinc. Therefore a solution of ferrocyanide containing appreciable amounts of ferricyanide exhibits a different zinc titer in the presence of hydrogen sulfide than in its absence.

The accepted method of standardizing solutions of ferrocyanide for use in zinc determination is to titrate in the absence of hydrogen sulfide. Scott[5] even goes so far as to state that its presence is not necessary. The author's experience is to the contrary.

A solution of ferrocyanide made in March 1924, and stored in an ordinary clear glass bottle in a cupboard, was standardized from time to time with the results shown in Table I.

TABLE I

| Date of standardization | Zinc value per cc. |
|---|---|
| March, 1924 | 0.00532 |
| Dec., 1924 | .00531 |
| Oct., 1930 | .00530 |
| Sept., 1931 | .00524 |

These values were all obtained with zinc oxide as the primary standard. The titrations were carried on in the presence of hydrogen sulfide under the same conditions of temperature, volume and acidity. At the time the last standardization was made duplicate samples of zinc oxide were titrated in the same manner but without the addition of hydrogen sulfide. The results of these titrations are listed in Table II.

The presence of ferricyanide in this solution was shown by its oxidizing action on potassium iodide. A fresh solution of ferrocyanide was prepared and standardized in the same manner. The results are given in Table II.

TABLE II

| ZnO, g. | $H_2S$ | Old ferrocyanide, cc. | New ferrocyanide, cc. |
|---|---|---|---|
| 0.2490 | None | 39.65 | 39.33 |
| .2490 | None | 39.60 | 39.30 |
| .2490 | Present | 38.20 | 39.18 |
| .2490 | Present | 38.18 | 39.15 |

It is therefore recommended that hydrogen sulfide be passed into the zinc solution during standardization and that the solution smell distinctly of the gas when the end-point is reached.

HOUGHTON, MICHIGAN

[5] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1927, 4th ed., p. 606B.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

# GALLIUM TRIETHYL MONOETHERATE, GALLIUM TRIETHYL, GALLIUM TRIETHYL AMMINE[1]

BY L. M. DENNIS AND WINTON PATNODE

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## Introduction

Of the elements of the third group in the Periodic Table, boron, aluminum and thallium are known to form normal alkyls, but those of gallium and indium have not hitherto been isolated.

The study of the possible preparation of gallium triethyl was begun several years ago in the Cornell Laboratory by H. A. Lovenberg. He added to a solution of ethylmagnesium bromide in ether, 45 g. of gallium bromide dissolved in 100 cc. of ether. The glass apparatus was of sealed joints throughout, and was kept filled with pure nitrogen during the experiment. The reaction was strongly exothermic, and the rate of addition of the gallium bromide was so adjusted that the ether refluxed quietly. After the addition of the gallium bromide, the mixture was further refluxed for thirty minutes. The condenser and dropping funnel were then sealed off from the flask and the stopcock on the inlet tube was closed. Mr. Lovenberg died shortly after this stage of the investigation was reached and the flask remained sealed until Mr. Patnode took up the examination of its contents in January of this year.

## Experimental

**Gallium Triethyl Monoetherate.**—The flask containing the reaction mixture just described was opened at the inlet tube for nitrogen, and the ether was drawn off by a pump until a sample of it, liquefied by solid carbon dioxide, became turbid upon the addition of very dilute ammonium hydroxide. All of the residual solution in the flask was then distilled in a current of carbon dioxide under a pressure of 30–40 mm. at 60–80°. The receiver was next attached by a normal slip-joint to a vacuum fractionation apparatus similar to that described by Laubengayer and Corey[2] except that the mercury valves were replaced by wide-bore stopcocks. The liquid was cooled to −50°, and the gas above it was pumped out. It was then gradually raised in temperature and was distilled into other bulbs of the chain by cooling them in liquid air. There were thus obtained two fractions, one volatile below −25° and the other above that temperature. The first fraction was chiefly ether and was discarded. The other portion was subjected to prolonged fractionation. There was finally obtained a liquid that had a vapor tension of somewhat less than 0.4 mm. Samples of this product were distilled into small (0.5 cc.) bulbs which were then sealed off from the chain and were used in the following experiments.

**Analysis.**—When one of the small sample bulbs was broken under ice-cold water,

[1] This article is based upon the thesis presented to the Graduate School of Cornell University by Winton Patnode in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1943 (1926).

drops of an oil-like substance were formed. On spectroscopic examination, these drops were found to be high in gallium and to contain no other metal. The water contained a trace of gallium but no other metal.[3]

In the analysis, one of the small sample bulbs was weighed, was then broken under cold water and the oily drops were dissolved by the addition of 6 *N* hydrochloric acid. The glass was collected on a filter and weighed. The acid solution was made strongly ammoniacal and 30% hydrogen peroxide was added. After standing for some hours, the solution was boiled until nearly all of the ammonia had been expelled, and the white, granular precipitate of gallium hydroxide was collected on an ashless filter, dried, ignited, treated with a few drops of concentrated nitric acid, again ignited and then weighed as gallium oxide in a stoppered weighing bottle.

Carbon and hydrogen were determined by combustion over copper oxide, one of the small weighed sample bulbs being broken in the combustion tube after the apparatus had been filled with nitrogen.

*Anal.* Calcd. for $Ga(C_2H_5)_3 \cdot (C_2H_5)_2O$: Ga, 30.19; H, 10.91; C, 51.97. Found: Ga, 30.64, 30.40; H, 10.60, 10.67; C, 50.34, 51.53.

These results, although not in close agreement with the calculated percentages, indicate that the substance is a monoetherate of gallium triethyl, and this conclusion is supported by a determination of the molecular weight of the compound by measuring the depression of the freezing point of benzene. This gave mol. wt., 232.8; calculated mol. wt., 230.9.

**Chemical Properties.**—Gallium triethyl monoetherate is a colorless liquid that is rapidly decomposed by moisture as already noted. In contact with air, dense white fumes are formed, and when dry oxygen was admitted to one of the small bulbs, the formation of the fumes was accompanied by a sharp report, a purple-colored flame and the deposition of a dark brown gum on the walls of the bulb. On breaking a bulb containing about 0.3 g. of the compound under 6 *N* nitric acid, the reaction was so violent as to break the Pyrex beaker and spray the acid to a distance of several feet.

Until quite recently, normal alkyls of trivalent thallium had eluded synthesis, one of the valences apparently differing from the other two, with the result that compounds of the type $Tl(alkyl)_2X$, salts of the strong base $Tl(alkyl)_2OH$, are formed.

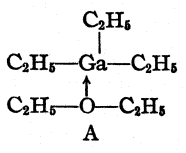
Gallium also exhibits a tendency to form compounds of the type $Ga(alkyl)_2X$, as was evidenced by the fact that when a sample of the etherate was broken under a measured volume of standard hydrochloric acid, and the evolved ethane was measured and the excess of the acid was titrated with sodium hydroxide, the results were approximately

$$Ga(C_2H_5)_3 \cdot (C_2H_5)_2O + HCl = Ga(C_2H_5)_2Cl + C_2H_6 + (C_2H_5)_2O.$$

The volume of the evolved ethane was somewhat greater than that called for in the equation, which indicates that $Ga(C_2H_5)_2OH$ is a much weaker base than the corresponding thallium compound.

[3] These spectroscopic analyses were made in this Laboratory by Professor Papish and his staff, to whom we wish to express our sincere appreciation of their invaluable assistance.

Gallium has a theoretical maximum covalency of six. In the monoetherate (A) the covalency would be four, the stability of the compound being due to the completely shared octet.



A

**Gallium Triethyl.**—Inasmuch as the reaction between gallium bromide and an ethereal solution of ethylmagnesium bromide yielded an etherate of the gallium alkyl, the possibility of the preparation of the simple alkyl by the action of mercury diethyl upon metallic gallium was next investigated.

Three small distilling bulbs, each of about 25 cc. capacity, were fused together in series, and the last bulb was attached to a fourth by a normal slip-joint carrying a glass stopcock, which permitted this fourth bulb to be closed and detached, and then connected with the vacuum fractionation apparatus.[2] Ten grams of metallic gallium was placed in the first bulb, and 2 g. in each of the next two. Fifty-two grams of mercury diethyl was run into the first bulb, the little chain was filled with nitrogen, and the necks of the three flasks, hitherto open, were sealed before the lamp. The first bulb was surrounded by a small air-bath and was very gradually raised in temperature up to 165° during a period of 200 hours. The bulb was then cooled, the nitrogen in the chain was pumped out, and the liquid in the first bulb was distilled, under diminished pressure, into the second bulb upon the 2 g. of gallium that it contained. The first bulb was then sealed off from the chain. Examination of the residual metal in the first bulb showed that it was nearly pure mercury, and its amount indicated that the reaction had proceeded practically to completion.

$$3Hg(C_2H_5)_2 + 2Ga = 3Hg + 2Ga(C_2H_5)_3$$

To make sure that all of the mercury diethyl had reacted with the gallium, the contents of the second bulb was heated for twenty-four hours at 120–125° and then for eighteen hours longer at about 150°. No change in the appearance of the colorless distillate or the bright metallic gallium resulted. The procedure was repeated by distillation into the third bulb, the second bulb was sealed off and the third bulb was heated for twenty-four hours longer. Again the absence of change in the appearance of the liquid or metallic gallium furnished quite conclusive evidence that the distillate contained no mercury diethyl.

The liquid was now distilled into the fourth bulb, the stopcock of this bulb was closed, and it was connected to the vacuum fractionation apparatus by the slip-joint. Its contents was held at 0°, and was separated into three fractions by distillation in the usual manner.[4] The middle fraction was used in the experiments described below.

**Analysis.**—A weighed sample of the liquid, contained in an evacuated bulb that was attached to the vacuum fractionation apparatus, was cooled with solid carbon dioxide, and an excess of 6 *N* sulfuric acid was added. The bulb was then allowed to warm up very slowly and was finally heated[5] to 90° for an hour. It was again cooled with

ANALYSES

| Sample, g. | Corr. vol. ethane, cc. Calcd. | Found | Ga, % Calcd. | Found |
|---|---|---|---|---|
| 0.2666 | 113.0 | 112.5 | ... | ... |
| .1775 | 75.2 | 75.2 | 44.45 | 44.13 |
| .3299 | 139.8 | 141.0 | 44.45 | 44.24 |

[4] Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924).

[5] This procedure is patterned after that employed by Laubengayer and Fleckenstein in the analysis of zinc ethyl, *Z. anorg. allgem. Chem.*, **191**, 283 (1930).

carbon dioxide, and the liberated gas was drawn off and measured. Combustion analysis showed it to be pure ethane. The gallium in the acid solution was determined by the method used by Dennis and Bridgman.[6]

Spectroscopic examination of the liquid showed it to be free from all metals but gallium.

**Molecular Weight.**—This was determined by the measurement of the depression of the freezing point of benzene.

| Sample, g. | Benzene, g. | Depression, °C. | Mol. wt. |
|---|---|---|---|
| 0.3382 | 43.8 | 0.15 | 263.5 |
| .2541 | 43.8 | .11 | 270.0 |
| .2778 | 43.8 | .12 | 270.0 |

The molecular weight of $Ga(C_2H_5)_3$ is 156.84. Consequently the above results show that the compound is associated in solution in benzene, which was to be expected since Roux and Louise[7] obtained similar results for aluminum ethyl in ethylene bromide.

**Density as Liquid.**—A sample of the alkyl was distilled into a bulb with a calibrated stem that made possible the measurement of volume with an accuracy of 0.005 cc. The bulb was held in a thermostat at 30° until the volume was constant, and was then weighed: density at 30°, 1.0576, 1.0583 g./cc.

**Melting Point.**—This was determined by the dropping ring method.[4] The average of two quite closely agreeing measurements was −82.3°.

**Vapor Tension.**—This was measured by the method of Dennis, Corey and Moore[4] from 0 to 144°. The vapor tension below 0° is too small to permit of accurate determination. The results of two experiments were in close agreement, and when plotted as the logarithm of the pressure against the reciprocal of the absolute temperature, gave a straight line. The equation of this line is

$$\log P = -2162 \times 1/T + 8.083$$

**Boiling Point.**—The boiling point as taken from the vapor tension curve is 142.6°.

**Chemical Properties.**—Gallium triethyl is a colorless, somewhat viscous liquid of unpleasant odor. It is spontaneously inflammable in the air, burning with a purple flame and producing a brown smoke. When a small, sealed bulb containing about 0.2 g. of the liquid was broken under cold water, there was a violent reaction which broke the Pyrex beaker and threw the water over a considerable area. With 95% alcohol instead of water, the reaction was somewhat less energetic. The alcoholic solution was slightly alkaline to litmus and to methyl orange, which indicated the formation of diethyl gallium hydroxide, a weak base.

[6] Dennis and Bridgman, THIS JOURNAL, **40**, 1531 (1918).

[7] Roux and Louise, *Bull. soc. chim.*, **50**, 511 (1888).

**Quantitative Reaction with Water.**—A weighed sample of the gallium alkyl was decomposed with water at room temperature in the same manner as described under Analysis, and the evolved ethane was measured. The liquid remaining in the bulb was added to an excess of standard hydrochloric acid, and the excess of acid was titrated with sodium hydroxide.

| | 0.1034 *N* HCl, cc. | | Corr. vol. ethane | |
|---|---|---|---|---|
| Sample, g. | Calcd. | Found | Calcd. | Found |
| 0.1655 | 10.20 | 10.22 | 23.35 | 23.1 |

These data indicate that the reactions proceed as follows

$$Ga(C_2H_5)_3 + H_2O = Ga(C_2H_5)_2OH + C_2H_6$$
$$Ga(C_2H_5)_2OH + HCl = Ga(C_2H_5)_2Cl + H_2O$$

**Gallium Triethyl Ammine.**—Theoretically, gallium triethyl should be capable of uniting with three molecules of ammonia, since gallium has a maximum covalency of six. Because of the stability of the completely shared octet, it was to be expected that one molecule of ammonia would be firmly held and form a quite stable compound. The results given below support this supposition. No experiments were made to ascertain whether more ammonia would enter into combination, but the evidence indicates that if the triammine were formed, it would readily lose two molecules of ammonia when subjected to diminished pressure.

To prepare the ammine, a weighed sample of the alkyl was brought into a bulb that was attached to the vacuum fractionation apparatus, the bulb was immersed in an ice-bath, and measured volumes of ammonia were admitted. The equilibrium vapor tension at 0° was measured after each addition. The pressure remained constant until one mole of ammonia for each mole of gallium triethyl had been added, and then rose rapidly, which indicated the formation of $Ga(C_2H_5)_3 \cdot NH_3$.

The product is a colorless liquid that is attacked only very slowly by the air. A few drops, exposed to the air overnight, changed to a white solid.

A drop of the liquid, held in a stream of oxygen, underwent no apparent change.

Small portions of the ammine, about 0.1 cc. each, were added to the following reagents in test-tubes.

(a) **Distilled Water.**—The sample sank to the bottom of the tube without visible reaction, but on standing for a few minutes, minute bubbles of gas which had the odor of ammonia were evolved. When the contents of the tube was heated, a white precipitate formed and an inflammable gas smelling strongly of ammonia was set free. The precipitate was soluble in dilute hydrochloric acid, and also in alcohol, to which it imparted an alkaline reaction. When this alcoholic solution was evaporated to dryness and the residue was dissolved in alcohol, the solution was still alkaline to litmus. These results indicate that the ammine is attacked by water with the evolu-

tion of ammonia and ethane, and the formation of diethyl gallium hydroxide.

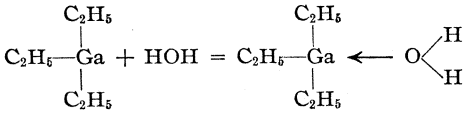
$$Ga(C_2H_5)_3{\cdot}NH_3 + H_2O = Ge(C_2H_5)_2OH + NH_3 + C_2H_6$$

(b) **Sulfuric Acid, 6N.**—Dropped into this reagent, the ammine was immediately decomposed, with the evolution of white fumes and an inflammable gas. A white precipitate that appeared at first dissolved when the acid was gently warmed, probably with the formation of diethyl gallium sulfate, $[Ga(C_2H_5)_2]_2SO_4$.

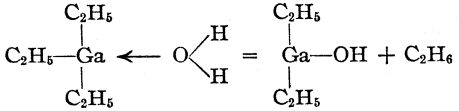
(c) **Potassium Hydroxide, Dilute Solution.**—The liquid ammine reacted slowly in the cold, and quite rapidly when warmed. Ammonia and an inflammable gas were given off. No precipitate appeared. This indicates that diethyl gallium hydroxide is amphoteric, and that it here formed $Ga(C_2H_5)_2OK$.

(d) The ammine was instantly dissolved by 95% alcohol, ether and benzene without apparent change in any case.

It is interesting to note that the simple gallium alkyl reacts violently with cold water, the etherate vigorously, and the ammine only very slowly. The reasons for these differences become obvious if the hydrolysis proceeds as follows. The first step may be assumed to be the coördination of a molecule of water



A molecule of ethane is then set free with the formation of diethyl gallium hydroxide.



The hydrolysis does not proceed further, and this is probably due to the insolubility of the product in water and to the fact that the gallium alkyls, resembling those of trivalent thallium as is to be expected, tend to form compounds in which one of the alkyl groups is replaced by hydroxyl or by an acid radical. But the position of gallium in the Third Group warrants the assumption that the univalent di-alkyl radical should be less stable than that of thallium, and this is confirmed by the fact that the thallium compounds are distinctly more stable in the presence of acids than is the gallium triethyl.

That hydrolysis of gallium triethyl etherate and gallium triethyl ammine proceeds more slowly than that of the normal alkyl, may be due to the fact that the fourth covalency is already occupied, in the one case by ether, and in the other by ammonia, and that hydrolysis cannot result

until either the ether or ammonia has been displaced by the water. That the ammine reacts more slowly than the etherate is explainable by the fact that in the ammine both the gallium and nitrogen have completely shared octets, while in the etherate only the gallium has a completely shared octet, that of oxygen still having an unshared lone pair.


## Summary

This article deals with the preparation and the properties of gallium triethyl monoetherate, gallium triethyl and gallium triethyl ammine. The behavior of the compounds upon hydrolysis is discussed in some detail, and evidence as to the existence of gallium diethyl hydroxide, a base, is presented. The latter substance is now being further investigated in the Cornell Laboratory.


ITHACA, NEW YORK

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF REED COLLEGE]

# STUDIES IN THE MEASUREMENT OF ELECTROMOTIVE FORCE IN DILUTE AQUEOUS SOLUTIONS. II. THE SILVER CHLORIDE ELECTRODE

BY WALTER R. CARMODY

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In a former paper[1] the writer discussed the importance of and difficulties involved in the measurement of electromotive force in dilute aqueous solutions and introduced a type of cell and a method designed to eliminate the relatively large variations in electromotive force encountered in such measurements. In the following paper this method has been applied to the measurement of the potential of the silver chloride electrode by means of the cell

$$Pt, H_2 (g), HCl, AgCl (s), Ag (s)$$

with such modifications of cell design and method as the problem necessitated.

Three investigators[2] have made measurements on this cell which permit extrapolation to be made to infinite dilution. Their results, although checking very well in concentrated solutions, diverge as the dilution is increased until at zero concentration they differ by as much as 1.0 mv. In each case glass has been used as material for cell and containers. Kraus and Parker[3] have shown that for strong acids, concentrations below 0.005 molar cannot be kept in glass containers without change, the relative effect of which increases with the dilution of the acid. Randall and

[1] Carmody, THIS JOURNAL, **51**, 2905 (1929).

[2] Noyes and Ellis, *ibid.*, **39**, 2532 (1917); Linhart, *ibid.*, **41**, 1175 (1919); Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926).

[3] Kraus and Parker, THIS JOURNAL, **44**, 2429 (1922).

Young[4] have pointed out the necessity of using quartz apparatus in determining the potential of the silver chloride electrode. They account for the discrepancy between results of electromotive force and freezing-point measurements by the action of the dilute acid solutions on the glass container which would cause a decrease in acid concentration and a corresponding increase in potential. Considering the electromotive force results to be high, they have estimated, from a summary of "freezing-point measurements of hydrochloric acid and the relation of these measurements to those of other salts," the value of the electrode potential to be $E^{\circ}_{298} = -0.2221$ volt. Results obtained from measurements made in quartz apparatus on eight concentrations of hydrochloric acid below 0.01 molar yield, upon extrapolation to infinite dilution, the value, $-0.2223$ volt.

## I. Electrodes and Materials

1. **The silver chloride electrodes** were prepared and used, with slight modification, according to the directions given by Carmody.[5] Platinum gauze electrodes 1.27 cm. square were electrolyzed as cathodes from a solution of potassium silver cyanide for a period of thirty hours with a current of two milliamperes per electrode. After being washed in distilled water for three weeks they were electrolyzed in the dark as anodes in dilute hydrochloric acid for one hour at a current of three milliamperes per electrode. This method usually produced pure white electrodes reproducible to 0.01 mv. On several occasions, for reasons undetermined, a light brown electrode was produced which gave a potential 0.2–0.3 mv. higher than that of the white electrodes. The brown electrodes corresponding to those produced and discarded by other investigators, were discarded in favor of the white electrodes, which have been found to be constant if kept in water or dilute hydrochloric acid from which oxygen has been removed. In acid solutions containing oxygen their potential lowers quite rapidly.

2. **The hydrogen electrodes** were prepared according to directions given by Popoff, Kunz and Snow.[6]

3. **The hydrochloric acid** solutions were prepared quantitatively from constant boiling acid distilled according to directions given by Foulk and Hollingsworth.[7] The concentrations were checked by analysis.

4. **Conductivity water,** with specific conductance below $1.0 \times 10^{-6}$ mhos, was used in preparing solutions. Water and all acid solutions below 0.05 molar were stored and used in quartz apparatus.

5. **Nitrogen** for stirring cells was purified by being passed through acid permanganate, alkaline pyrogallol, water and finally through a solution of the same concentration as used in the cell.

6. **Hydrogen** used in the hydrogen electrode was prepared in a U-tube generator similar to that used by Lewis, Brighton and Sebastian.[8] As an added precaution an auxiliary cathode was used in the anode compartment as suggested by Niese.[9] The

[4] Randall and Young, THIS JOURNAL, **50,** 989 (1928).
[5] Carmody, *ibid.*, **51,** 2901 (1929).
[6] Popoff, Kunz and Snow, *J. Phys. Chem.*, **32,** 1056 (1928).
[7] Foulk and Hollingsworth, THIS JOURNAL, **45,** 1220 (1923).
[8] Lewis, Brighton and Sebastian, *ibid.*, **39,** 2245 (1917).
[9] Niese, *Physik. Z.*, **24,** 12 (1923).

auxiliary cathode serves to prevent diffusion of oxygen into the hydrogen supply and eliminates the necessity of using sand for that purpose.

## II. Apparatus and Method

The cell (Fig. 1) was of quartz except for the central three-way stopcock, reservoir stoppers and cell electrodes, which were of Pyrex glass. Connections to the several parts of the cell were ground joints requiring no lubrication. During the interval necessary for the cell to reach equilibrium the solution came in contact at times with the end of the Pyrex tube to which the electrodes were sealed. Any change of concentration due to this slight contact was considered to be negligible. The cell was designed with small electrode compartments (25 cc.) with large connecting reservoirs (500 cc.). The electrodes were placed in separate compartments to permit the study of the silver chloride electrode independently of the hydrogen electrode. The method of measurement was as follows.

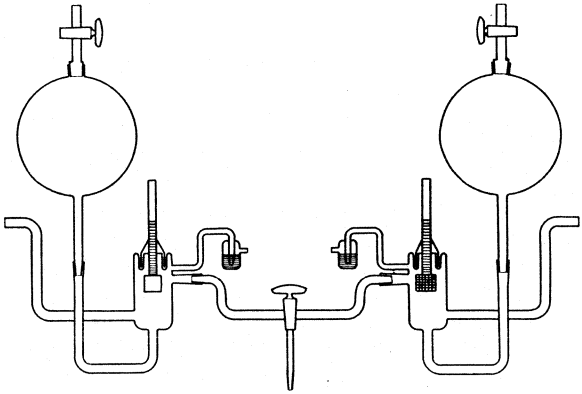

Fig. 1.—Quartz cell.

The cell, with electrodes in position, and reservoir are filled with the oxygen-free solution and seasoned by standing for several hours, when the solution is drawn off and the reservoirs filled with a new supply. The electrode compartments are then washed at intervals with this fresh solution. After final washing and filling the hydrogen is bubbled through the hydrogen electrode compartment while the silver chloride compartment is stirred with nitrogen. After the cell has reached equilibrium a second measurement may be made readily by filling the electrode compartments with a new supply of solution from the reservoir and obtaining a new equilibrium.

## III. Experimental

To test the constancy of the potential of the silver chloride electrode in water and in hydrochloric acid three groups of electrodes were allowed to stand for two weeks: one group in water, one group in dilute hydrochloric acid freed from oxygen and one group in dilute hydrochloric acid in contact with air. Checking against a group of freshly prepared electrodes showed no change in the electrodes which had stood in water and in hydrochloric acid freed from oxygen, while those electrodes which had stood in hydrochloric acid in contact with air were 0.6 to 0.7 mv. positive. Throughout the experiment electrodes stored in water and used with

oxygen-free hydrochloric acid solution suffered no apparent change in appearance or potential.

With the hydrogen electrode at equilibrium a study was made of the time and conditions necessary to establish and maintain stable equilibrium in the silver chloride compartment. With pure hydrochloric acid in the compartment a period of about four hours was necessary to establish equilibrium, during which time the potential rose approximately 6.0 mv. This equilibrium, however, was quite unstable, being easily disturbed by any motion between electrode and surrounding solution, which would cause the potential to lower to nearly its original value. With hydrochloric acid that had been previously saturated with silver chloride, a somewhat shorter time was found necessary for equilibrium to be established. This equilibrium was relatively stable and independent of small motions between electrode and solution. In the measurements described below the hydrochloric acid was saturated with silver chloride before being introduced into the silver chloride compartment, and stable equilibrium was obtained in each measurement recorded.

Measurements were made first at concentrations above 0.01 molar to compare the silver chloride electrodes with those used by other investigators; then at concentrations from 0.01 molar to 0.0003 molar, which limit was determined by the apparatus available. Results are shown in Table I. The molalities are given in column 1, the two most dilute of which are corrected for the solubility of the silver chloride in hydrochloric acid. Calculations were based on the solubility measurements of Forbes and Cole.[10]

TABLE I

ELECTROMOTIVE FORCE AT 25° OF THE CELL: Pt, $H_2(g)$, HCl, AgCl(s), Ag(s)

| Molality, $m$ | $E$ measured | $E^{\circ\prime}$ $E + 0.1183 \log m$ |
|---|---|---|
| 0.1165 | 0.3449 | −0.2344 |
| .1083 | .3483 | − .2341 |
| .1056 | .3496 | − .2341 |
| .09425 | .3552 | − .2338 |
| .04572 | .3901 | − .2316 |
| .009582 | .4660 | − .2272 |
| .004965 | .4987 | − .2261 |
| .002799 | .5271 | − .2251 |
| .001910 | .5462 | − .2245 |
| .001129 | .5727 | − .2241 |
| .0007280 | .5950 | − .2238 |
| .0005518 | .6090 | − .2236 |
| .0003288 | .6353 | − .2233 |

For purposes of extrapolation we may use the equation of Lewis and Randall, $E^\circ = E^{\circ\prime} + 0.1183 \log \gamma$ where $E^{\circ\prime} = E + 0.1183 \log m$. The

[10] Forbes and Cole, THIS JOURNAL, **43**, 2492 (1921).

third column of Table I contains the values of $E^{\circ\prime}$ calculated from experimental results. In Fig. 2 these are plotted against the square root of the molality. For comparison the numerous points of other investigators are indicated. Extrapolation to zero concentration of the new experimental values yields the result: Ag (s), AgCl (s), $Cl^-$: $E^{\circ}_{298} = -0.2223$ volt. This value corresponds closely to that estimated by Lewis and Randall.[4]

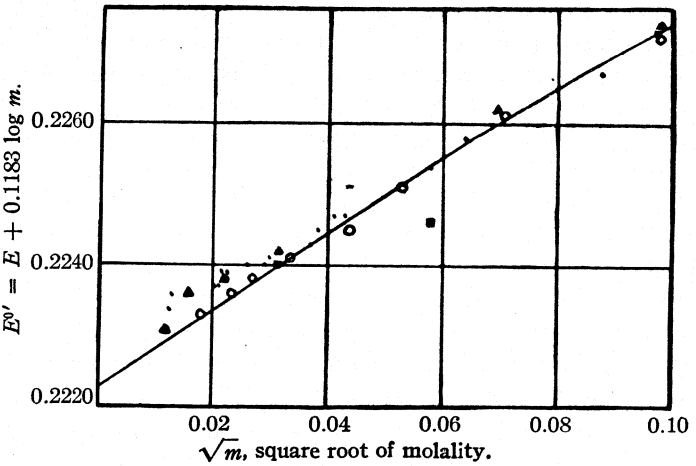


Fig. 2.—Curve showing $\sqrt{m}$ plotted against $E^{\circ\prime}$ for the cell, Pt, $H_2$ (g), HCl, AgCl (s), Ag (s), at 25°: △, Linhart; □, Noyes and Ellis; •, Nonhebel; ○, Carmody.

The writer is pleased to acknowledge his indebtedness to Dr. H. V. Tartar and to the Chemistry Department of the University of Washington for apparatus and materials and for the privileges of the laboratory in which the experimental work described in this paper was completed.

## IV. Summary

1. The electromotive force of the cell, Pt, $H_2$ (g), HCl, AgCl (s), Ag (s), has been measured with quartz apparatus at eight concentrations below 0.01 molar.

2. From these measurements a new value for the potential of the silver chloride electrode has been obtained: $E^{\circ}_{298} = -0.2223$ v.

PORTLAND, OREGON

[CONTRIBUTION FROM THE BOWNE HALL OF CHEMISTRY, SYRACUSE UNIVERSITY]

# A PHASE STUDY OF THE SYSTEM AMMONIA–HYDROGEN SULFIDE

BY LEOPOLD SCHEFLAN AND C. R. MCCROSKY

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With the exception of ammonium hydrosulfide, the existence of pure compounds of ammonia and hydrogen sulfide has not been definitely established although a considerable number have been reported by various investigators. The following compounds have been described in the literature: $NH_2HS$,[1,2,3,4,5,6] $(NH_4)_2S$,[1,6,7,8,9,10] $(NH_4)_2S\cdot(NH_3)_2$,[4] $(NH_4)_2S\cdot(NH_3)_4$,[9] $(NH_4)_2S\cdot NH_4HS$,[2,5] $(NH_4)_2S\cdot(NH_4HS)_2$,[2,5] $(NH_4)_2S\cdot(NH_4HS)_2\cdot(H_2O)_x$,[2,5] $(NH_4)_2S\cdot(NH_4HS)_{12}$,[2,5] $(NH_4)_2S\cdot(NH_4HS)_{18}\cdot(H_2O)_4$,[2,5] $(NH_4)_2S\cdot(NH_4HS)_{24}$.[2,5,11]

Unfortunately, reports which give methods of preparing these substances with the exception of $NH_4HS$ are vague and sometimes contradictory. In most cases it would appear that the methods which the older investigators used could not have yielded compounds in a pure state.

Scheffer[12] investigated the dissociation equilibrium of the system ammonia–hydrogen sulfide, determining the critical constants of ammonia and hydrogen sulfide, and the three phase line of the compound $NH_4HS$ at which solid, liquid and vapor are in equilibrium with one another.

With the object of obtaining more definite knowledge concerning the nature of the compounds formed between ammonia and hydrogen sulfide, it seemed worth while to make a study of the vapor pressure and the freezing points of mixtures of these substances.

## Experimental Procedure

The method of Foote and Brinkley[13] was used in preparing dry ammonia. The pure gas was passed into a flask partly filled with ammonium thiocyanate, which deliquesces and acts as an absorbent. By cooling the flask with ice during the process of absorption, it is possible to get a solution which contains about 45% of ammonia.

[1] Bineau, *Ann. chim. phys.*, **67**, 225–251 (1839); **68**, 416–441 (1839).

[2] Bloxam, *J. Chem. Soc.*, **67**, 277–309 (1895).

[3] Naumann, *Ber.*, **43**, 313–321 (1910).

[4] Troost, *Compt. rend.*, **88**, 1267 (1879).

[5] Bloxam, *Chem. News*, **68**, 97–98 (1893).

[6] Thomas and Riding, *J. Chem. Soc.*, **123**, 1181–1189 (1923).

[7] Bineau, *Ann. chim. phys.*, **70**, 251–272 (1839); **32**, 227–232 (1839).

[8] Bineau, *Berz. J.*, [2] **20**, 137–138 (1839).

[9] Maumené, *Compt. rend.*, **89**, 506–507 (1879).

[10] Deville, *ibid.*, **88**, 1239–1240 (1879).

[11] Fritsche, *J. prakt. Chem.*, **24**, 460–467 (1841); **32**, 313–317 (1844).

[12] Scheffer, *Z. physik. Chem.*, **71**, 671–704 (1910); **76**, 161–173 (1911).

[13] Foote and Brinkley, THIS JOURNAL, **43**, 1178–1179 (1921).

This flask was sealed to the apparatus as shown in Fig. 1. The gas liberated from A is further dried by passing it over sodium. This metal reacts with gaseous ammonia at elevated temperature but not appreciably at room temperature. Samples of the gas were drawn out after this treatment and analyzed, and found to be free from moisture, non-condensable gases and solid impurities. It was also solidified with liquid air and the melting points were determined. In each case the melting point agreed within less than 1° with that reported in the literature for pure ammonia.

Hydrogen sulfide was prepared by the action of dilute sulfuric acid on pure sodium sulfide and dried over calcium chloride and phosphorus pentoxide. It also proved to be advisable to condense it in a bath of carbon dioxide and ether. By this procedure the hydrogen sulfide could be stored and any moisture frozen out. Samples of the purified gas were found to be free from moisture and solid impurities. When dissolved in sodium hydroxide solution and analyzed, it was found to contain no chloride, nitrite or nitrate ions. Samples of the gas were solidified with liquid air and the melting points were found to agree within less than 1° with the temperature reported for pure hydrogen sulfide.

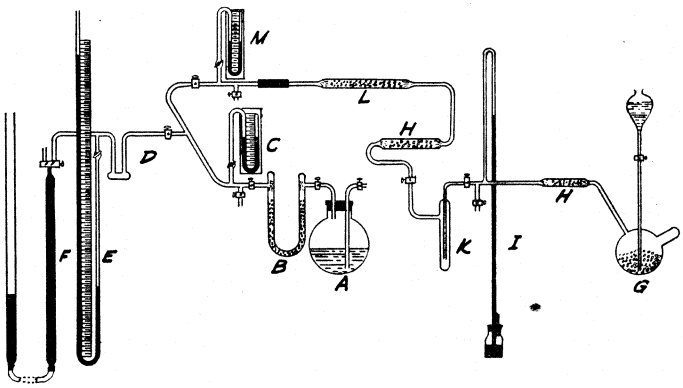


Fig. 1.—Vapor pressure apparatus.

The essential features of the apparatus used in the first part of the work are shown in Fig. 1. The ammonia branch begins with the flask (A) containing the ammonia–ammonium thiocyanate solution. The ammonia is passed over sodium (B) for drying. A manometer (C) and an outlet are included. The hydrogen sulfide branch begins with the flask (G) containing sodium sulfide. A separatory funnel containing dilute sulfuric acid is sealed through this flask. The glass tubing coming from the generator leads to a safety outlet, a manometer (I), calcium chloride tubes (H), a condensing tube (K) from which the hydrogen sulfide can be boiled off whenever necessary, and a phosphoric anhydride tube (L). The two branches meet near the reaction chamber. The gases are condensed in the reaction chamber (D) cooled from the outside with a suitable bath of liquid air or carbon dioxide and ether, and the pressure read on a manometer. The concentration of the mixture is varied by means of the mercury pump made from an ordinary gas buret. Before collecting a sample each half of the apparatus was thoroughly swept out with its own gas.

Ammonia was first condensed in the reaction chamber, which was surrounded by a freezing mixture of solid carbon dioxide and ether. After shutting off the ammonia stream, hydrogen sulfide was admitted, resulting in the formation of a white solid which melted to a clear liquid when the reaction chamber was surrounded by the ice-water bath. Ammonia was withdrawn from the system a number of times and after equi-

librium had been reached the successive pressures were read. From the data obtained, the vapor pressure diagram for 0° was constructed.

The vapor pressure–temperature curve of the three phase system $NH_4HS$ (solid), solution, and vapor, was determined by two methods. (1) Equilibrium was established at 0° with crystals in contact with the solution. The ice-water bath was then replaced by baths of various temperatures, and the pressures were noted. Temperatures below 0° were obtained with salt–ice–water and ice–alcohol mixtures. The desired low temperature was held for a period of time by careful additions of small amounts of alcohol or ice to the well insulated bath. Temperatures above 0° were obtained by mixing hot and cold water. (2) Mixtures of ammonia and hydrogen sulfide were liquefied in a freezing mixture and then immersed in a bath of the desired temperature. Ammonia was pumped off until crystals appeared, and the constant pressure was recorded.

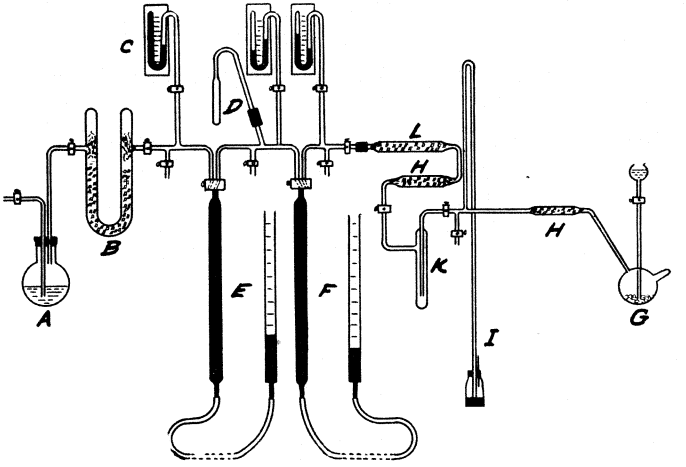


Fig. 2.—Freezing point apparatus.

Figure 2 shows the apparatus used for the determination of the freezing point curve of the system $NH_3 \cdot H_2S$. Ammonia was measured out in known quantities through the gas buret E into the reaction chamber D, which was cooled by the carbon dioxide–ether mixture. After the desired quantity of ammonia had condensed, the quantity of hydrogen sulfide necessary for the particular sample was measured in through the gas buret F from the tube K. In this way the desired mixture was collected in the reaction chamber. Then the sample was frozen and the reaction chamber sealed off. All tubes were approximately the same size: 15 cm. long and 1 cm. inside diameter.

The freezing point of each mixture was determined by using the method employed by Rupert.[14] This method of determining freezing points was checked by determining the freezing points of hydrogen sulfide, water, and acetamide. In each case the freezing point found checked closely with the accepted values for these substances. The thermometers were corrected by comparing them with thermometers calibrated by the Bureau of Standards.

## Experimental Results

**The Vapor Pressure Diagram of 0°.**—In Table I are the data from which the curve in Fig. 3 was drawn. In this curve it is to be noted that

[14] Rupert, THIS JOURNAL, **31**, 851–866 (1909).

there are only two regions of constant pressure at 0°. The crystals which separated out at the first constant pressure region were analyzed and found to have a ratio of $NH_3$ and $H_2S$ corresponding to the composition of $NH_4HS$, as shown in Table II.

The analysis was performed in the following manner. As soon as the liquid phase had disappeared from the tube and the pressure had just begun to drop, the reaction chamber was sealed off from the rest of the apparatus. The tube was weighed and chilled in the cooling mixture of carbon dioxide and ether, which greatly decreased the pressure within the tube, and allowed it to be broken under ice cooled water in a closed vessel. In this way, samples with high vapor pressure could be dissolved with negligible

TABLE I

TEMPERATURE OF BATH, 0° ATMOSPHERIC PRESSURE, 740 MM. MANOMETER READINGS, MM.

| Gas removed, cc. | Left, mm. | Right, mm. | Difference, mm. | Absolute pressure, mm. |
|---|---|---|---|---|
| 0 | 210.0 | 815.0 | 605 | 1345 |
| 40.0 | 282.0 | 740.0 | 460 | 1200 |
| 26.0 | 320.0 | 701.0 | 381 | 1121 |
| 25.5 | 368.0 | 657.0 | 289 | 1029 |
| 25.0 | 402.5 | 623.5 | 221 | 961 |
| 20.5 | 436.5 | 591.5 | 155 | 895 |
| 24.5 | 465.0 | 562.0 | 97 | 837 |
| 45.5 | 465.0 | 563.0 | 98 | 838 |
| 65.4 | 465.0 | 562.0 | 97 | 837 |
| 50.7 | 465.0 | 562.0 | 97 | 837 |
| 36.0 | 466.0 | 562.0 | 96 | 836 |
| 45.8 | 466.0 | 562.0 | 97 | 837 |
| 40.3 | 466.0 | 562.0 | 97 | 837 |
| 40.4 | 522.0 | 507.0 | − 15 | 725 |
| 30.3 | 610.0 | 416.0 | −194 | 546 |
| 25.4 | 708.5 | 318.5 | −390 | 320 |
| 30.2 | 722.5 | 253.5 | −519 | 221 |
| 20.2 | 843.0 | 183.0 | −660 | 80 |
| 45.4 | 843.0 | 183.0 | −660 | 80 |
| 40.1 | 853.0 | 183.0 | −670 | 79 |
| 35.3 | 843.0 | 183.0 | −660 | 80 |
| 25.6 | 843.0 | 183.0 | −660 | 80 |

TABLE II

ANALYSIS OF CRYSTALS FROM THE FIRST CONSTANT PRESSURE REGION (840 MM.)

| Sample | $NH_3$, % | $H_2S$, % |
|---|---|---|
| I | 34.70 | 63.75 |
| II | 34.53 | 63.56 |
| III | 33.31 | 63.98 |
| IV | 33.10 | 63.77 |
| V | 33.65 | 64.43 |
| VI | 33.43 | 64.01 |

Theoretical value for $NH_4HS$, 33.36

loss. This solution was diluted to a definite volume and aliquot parts were taken for analysis. The remnants of the reaction chamber were carefully collected and weighed. One portion of the solution was run into an excess of acidified standard iodine solution, titrated with sodium thiosulfate solution, and the hydrogen sulfide content calculated.

The ammonia content was determined by titrating another portion with standard sulfuric acid, using methyl orange as an indicator. In every analysis the value obtained for hydrogen sulfide was a little lower than the theoretical value. Undoubtedly the cause for this discrepancy is the escape of small amounts of hydrogen sulfide gas, preceding and during the titration. The odor of hydrogen sulfide was distinctly noticeable in each solution analyzed.

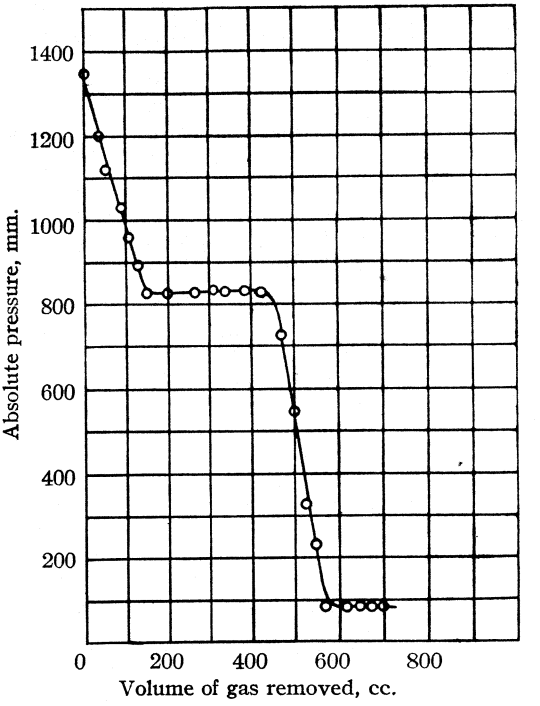


Fig. 3.—Vapor pressure curve system: $NH_3$–$H_2S$ at 0°.

Table III shows the results of the two methods which were used to determine the vapor pressure–temperature curve of the three phase system ammonium hydrosulfide (solid), solution, and vapor. Figure 4 gives this curve as calculated by averaging the results of both methods.

The values obtained for the freezing points of the various mixtures are given in Table IV and the curve constructed from the data in this table is given in Fig. 5. Two peaks are noted in this curve, corresponding to the composition of $(NH_4)_2S$ and $NH_4HS$. Analysis of crystals removed from the region of the first peak shows them to approximate very closely the composition of $(NH_4)_2S$, as shown in Table V. Crystals removed at the second peak or higher melting point have a composition closely corresponding to $NH_4HS$ as shown in Table VI.

## Discussion

The curve drawn in Fig. 3 differs slightly from the one required by the theory as there should be a vertical line between the two horizontal lines.

TABLE III

VAPOR PRESSURES OF THE THREE PHASE SYSTEM $NH_4HS$ (SOLID), LIQUID AND VAPOR

| Temp., °C. | Vapor pressure, mm., determined by Method 1 | Method 2 | Average |
|---|---|---|---|
| −21 | 434 | 437[a] | 435.5 |
| −12 | 547 | 550 | 548.5 |
| −10 | 582 | 580 | 581.0 |
| − 7.8 | 604 | 605 | 604.5 |
| − 7.5 | 633 | 630 | 631.5 |
| − 5.9 | 663 | 665 | 664.0 |
| − 5 | 687 | 685 | 686.0 |
| − 4 | 707 | 710 | 708.5 |
| − 2.5 | 779 | 781 | 780.0 |
| 0 | 839 | 837 | 838.0 |
| 2.5 | 917 | 918 | 917.5 |
| 5 | 1004 | 1000 | 1002.0 |
| 6 | 1077 | 1073 | 1075.0 |
| 7.5 | 1118 | 1122 | 1120.0 |
| 9 | 1200 | 1203 | 1201.5 |
| 10 | 1248 | 1245 | 1246.5 |

[a] This particular pressure was determined by Dr. Aden J. King of this Laboratory.

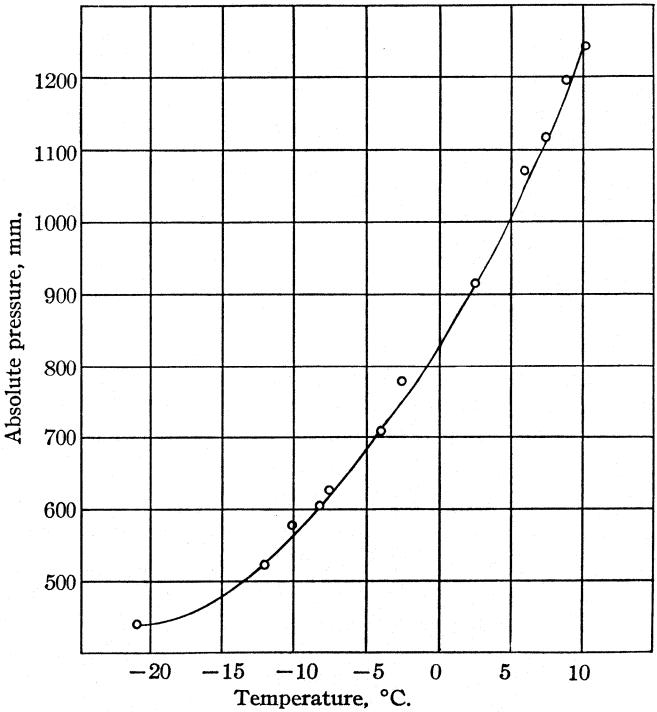


Fig. 4.—Vapor pressure–temperature curve system: ammonium hydrosulfide (solid)–solution–vapor.

TABLE IV

RESULTS OF TWO METHODS

| % $NH_3$ by vol.[a] | % $H_2S$ by vol.[a] | Melting temp., °C. | | | | Average temp., °C. |
|---|---|---|---|---|---|---|
| 100.0 | 0.0 | −77 | −79 | −78 | −78 | −78.0 |
| 97.5 | 2.5 | −85 | −84 | −82 | −83 | −83.5 |
| 95.0 | 5.0 | −89 | −86 | −88 | −89 | −88.0 |
| 92.5 | 7.5 | −73 | −73 | −72 | −71 | −72.3 |
| 90.0 | 10.0 | −59 | −60 | −61 | −60 | −60.0 |
| 87.5 | 12.5 | −48 | −49 | −48 | −48 | −48.3 |
| 85.0 | 15.0 | −38 | −39 | −37 | −39 | −38.2 |
| 82.5 | 17.5 | −31 | −30 | −29 | −30 | −30.0 |
| 80.0 | 20.0 | −22 | −22 | −23 | −23 | −22.5 |
| 77.5 | 22.5 | −19 | −20 | −20 | −18 | −19.2 |
| 75.0 | 25.0 | −17 | −18 | −18 | −19 | −18.0 |
| 72.5 | 27.5 | 11 | 11 | 11 | 12 | 11.2 |
| 70.0 | 30.0 | 39 | 41 | 40 | 41 | 40.2 |
| 67.5 | 32.5 | 63 | 62 | 62 | 62 | 62.2 |
| 65.0 | 35.0 | 78 | 78 | 80 | 80 | 79.0 |
| 62.5 | 37.5 | 91 | 92 | 92 | 92 | 91.8 |
| 60.0 | 40.0 | 101 | 100 | 101 | 101 | 100.8 |
| 57.5 | 42.5 | 105 | 104 | 106 | 106 | 105.2 |
| 55.0 | 45.0 | 114 | 114 | 115 | 115 | 114.5 |
| 52.5 | 47.5 | 116 | 117 | 117 | 117 | 116.8 |
| 50.0 | 50.0 | 118 | 118 | 117 | 119 | 118.0 |
| 47.5 | 52.5 | 118 | 118 | 117 | 119 | 118.0 |
| 0 0 | 100.0 | −83 | −83 | −84 | −84 | −83.5 |

[a] These numbers are equivalent to 100 times the mole fraction.

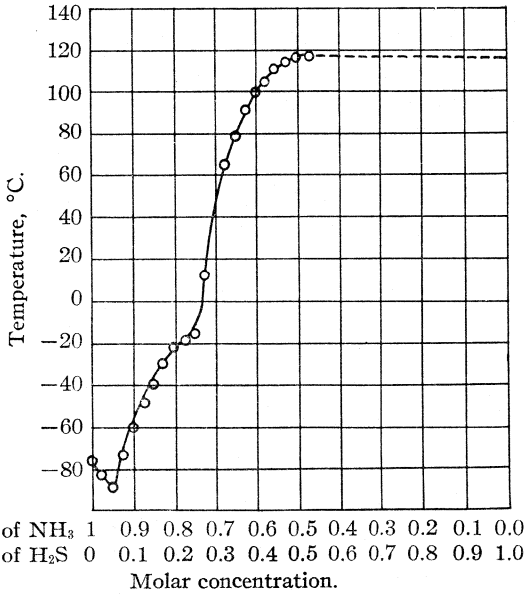


Fig. 5.—Freezing point curve system for $NH_3$–$H_2S$.

TABLE V

ANALYSIS OF LOW MELTING POINT CRYSTALS

| Sample | $NH_3$, % | $H_2S$, % |
|---|---|---|
| I | 52.03 | 47.22 |
| II | 51.87 | 48.11 |
| III | 52.24 | 47.46 |
| IV | 51.99 | Lost |
| V | 52.47 | 47.39 |
| Theoretical value for $(NH_4)_2S$ | 50.06 | 49.94 |

TABLE VI

ANALYSIS OF HIGH MELTING CRYSTALS

| Sample | $NH_3$, % | $H_2S$, % |
|---|---|---|
| I | 34.71 | 63.87 |
| II | 34.92 | 64.10 |
| III | 35.02 | 64.23 |
| IV | 34.29 | 63.98 |
| V | 34.66 | 64.26 |
| Theoretical value for $NH_4HS$, | 33.36 | 66.64 |

When the liquid phase disappeared and more and more ammonium hydrogen sulfide crystallized, the time necessary for the establishment of the equilibrium increased greatly.

On pumping off ammonia at a definite rate, once the liquid phase had disappeared, another region of constant pressure was reached. This is noted in the second flat portion of the curve at a pressure of 80 mm. This, therefore, is taken as the dissociation pressure of ammonium hydrogen sulfide at 0°.

During the two periods of constant pressure the gas was removed at various rates. This change of the velocity had no effect on the pressure.

The latter part of the curve agrees with the results of two other investigators. Walker and Lumsden[15] worked on the dissociation pressure of ammonium hydrogen sulfide at temperatures higher than 0°, determining the vapor pressure–temperature curve for this salt. By interpolating their curve to 0°, a value of a little more than 80 mm. is obtained, in close agreement with our value.

The vapor pressure–temperature curve of the three phase system $NH_4HS$ (solid), liquid, and vapor was found to be convex to the temperature axis. This is in agreement with the general rule.

Table III shows that the freezing points of various mixtures having the same composition agree nearly always within 2°. In this type of work such agreement is close enough to indicate the existence of compounds and eutectics.

The melting point of $NH_4HS$, which was found to be 118°, agrees with the temperature as given by earlier investigators. E. Briner[16] found that

[15] J. Walker and J. S. Lumsden, *J. Chem. Soc.*, **71**, 428–440 (1897).

[16] E. Briner, *Compt. rend.*, **142**, 1216–1218 (1906).

the melting point of $NH_4HS$ in a closed vessel was 120°, while F. E. C. Scheffer[13] obtained the value of 118°.

The literature contains conflicting statements regarding the existence and stability of ammonium sulfide, $(NH_4)_2S$. Bineau[1,7] obtained it by mixing two volumes of ammonia with one volume of hydrogen sulfide at a temperature of −18°. He said that it was stable only at low temperatures and that it easily dissociated into $NH_3$ and $NH_4HS$. St.-Claire Deville[10] found that it was not decomposed at a temperature of 90°. Bloxam[5] repeated Bineau's work, but failed to prepare $(NH_4)_2S$ by Bineau's method. Instead of getting ammonium sulfide, he always obtained mica-like crystals of the composition $(NH_4)_2S\cdot(NH_4HS)_n$ or an oily liquid of the composition $(NH_4)_2S\cdot(NH_3)_2$. He states that by carefully regulating the volumes of the gases and their rates of flow he succeeded in obtaining micaceous crystals of ammonium sulfide. From this description, however, it seems very probable that his crystals were always more or less contaminated with ammonium hydrosulfide. Thomas and Riding[6] were unable to obtain ammonium sulfide by Bloxam's method. The following is quoted from their article: "Anhydrous ammonium hydrosulfide is best prepared by alternately passing ammonia and hydrogen sulfide into dry ether. Attempts to convert the hydrosulfide into the monosulfide by prolonged action of saturated solutions of ammonia in ether failed, but in the presence of a small quantity of alcohol a yellow oil having the composition $(NH_4)_2S\cdot(NH_3)_2$ separated out, together with a few transparent crystals, believed to be anhydrous ammonium sulfide. Similar crystals were obtained when the oil was kept in an iron vessel. The ratio $NH_3/H_2S$ was determined for these crystals, the results lying between 1.92 and 2.11."

Our own results indicate that ammonium sulfide must be unstable under ordinary conditions. It has a high dissociation pressure and must decompose very rapidly. This is in agreement with the results of Thomas and Riding. However, their report does not indicate in any way that they succeeded in isolating this compound at room temperature. They weighed and analyzed a rapidly decomposing substance of unknown purity. Therefore their results seem to be questionable.

## Summary

1. The vapor pressure curve of the system $NH_3$–$H_2S$ has been determined at a temperature of 0°.

2. Two regions of constant pressure were obtained: one at a pressure of 80 mm., the other at a pressure of 837 mm. The first pressure represents the dissociation pressure of $NH_4HS$ at 0° while 837 mm. is the pressure at which the solid compound is in equilibrium with solution and vapor at the same temperature.

3. The dissociation pressure of $NH_4HS$ checks with the pressure which

can be predicted from the dissociation pressure–temperature curve of $NH_4HS$ as determined by Walker and Lumsden.

4. The temperature–concentration phase diagram of the system $NH_3$–$H_2S$ was determined.

5. The diagram indicates the existence of two compounds $NH_4HS$ and $(NH_4)_2S$ and a eutectic mixture of 95% $NH_3$ and 5% $H_2S$.

6. Solid crystalline $(NH_4)_2S$ does not exist above $-18°$. On heating, at this temperature, it decomposes into solid crystalline $NH_4HS$ and melt.

7. The melting point of $NH_4HS$ agrees with the temperature as given by earlier investigators.

8. The vapor pressure curve in this work shows that probably only one compound, ammonium hydrosulfide, is stable above 0°.

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

# INTERFERENCE OPTICAL LEVER FOR PRESSURE GAGES, GALVANOMETERS, ETC.

BY W. E. ROSEVEARE

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It is possible, with a very simple optical system, to measure deflections with an average error corresponding to about 0.001 mm. for a meter optical arm. The optical system is shown in Fig. 1. The usual galvanometer lamp was replaced by a very narrow slit S and two slit apertures S″ were placed in front of the projection lens P. The projected image of the slit, viewed through an eyepiece or microscope, consisted of a number of straight interference bands with nearly all the light in the three center bands. The source of light L was a 100-watt frosted light bulb placed in a lamp house with a 1-cm. hole in the side to illuminate the slit. The collimator of an old spectroscope was used for the narrow slit and lens. The slit must be one that equally illuminates the two slit apertures when the former is made very narrow. Some spectroscope slits were found to be shaped like A and B of Fig. 1. They were unsuitable and were ground to the shape C or D on a fine oil stone. Projection lenses with a focal length of 15–17 cm. were found most convenient for use with a two or three meter optical lever. The slit apertures were 3 mm. wide and 3 mm. apart and about 20 cm. from the mirror M. A filar micrometer eyepiece was used for measuring deflections up to 1 cm., while a comparator was used for measuring deflections up to 10 cm. The cross hair was always set in the center of the most intense interference band. The mirror must be of good quality plate glass and should be $^3/_8$-inch size. Some

galvanometer mirrors were not sufficiently plane and therefore it was necessary to select a good mirror. Five $^3/_8$-inch mirrors were tested and all were found to be satisfactory, while all $^1/_2$-inch mirrors tested were found to be useless.

By the following systematic procedure it was easy to set up and adjust the optical system. With the room dark and the slit open about 0.5 mm., an image of the latter was focused on a white paper in the position where the eyepiece was to be placed. A piece of paper was held in the path of the light a short distance from the mirror at the position indicated by the dotted line F. This showed two spots of light. The mirror or "collimator" was moved sidewise until the two spots were the same size. If the amount of light on both sides was not nearly the same, the interference bands were overcast by white light. The eyepiece was then put in place and the slit closed until 0.02 mm. wide. Two images of the slit appeared when the slit was not in focus and the slit was moved back and forth until these two images coincided. Interference bands were then usually observed. If sharp interference bands were not observed, it was due either to the slit being too wide or improperly shaped, or the mirror not being plane enough. In such a case, the mirror was replaced by a large plate glass mirror and the slit placed out of focus. The intensity of the two images of the slit should be the same when the slit is 0.02 mm. wide. If not, the slit should be ground to the proper shape. The galvanometer mirrors were then tested after it was known that the rest of the system was in good adjustment. During the adjustments, care had to be taken to keep the openings of the slit and slit apertures parallel. After the adjustments had been made, it was not necesary to have the room dark since the bands could easily be seen in a room with ordinary illumination. However, there should not be any lights shining directly on the eyepiece lens or it will obscure the interference bands. A telescope tube, attached in front of the eyepiece, cut down stray light and made observation much easier. A very much brighter image was obtained by using a point-o-light lamp with condensing lens to illuminate the slit, but more care was required to get equal intensity of light through the two slit apertures.

**Sensitivity of Optical Lever.**—In order to test the sensitivity of the optical lever, a series of twenty successive readings was taken with the mirror in a fixed position. Table I gives the results in terms of deviation

TABLE I

RESULTS

| | | | |
|---|---|---|---|
| −2 | 0 | +6 | −4 |
| +7 | −7 | −1 | +6 |
| −4 | −9 | 0 | −1 |
| −1 | +4 | +1 | −1 |
| −1 | +5 | −5 | −1 |

from the mean reading in $10^{-3}$ mm. The average deviation from the mean is 0.0033 mm. for a 3-meter lever arm, which corresponds to 0.0011 mm. for a meter distance. The sensitivity may be increased by having the double slits farther apart, thus making the interference bands narrower. In that case, better lenses and a larger mirror are required to give good results.

**Pressure Gage.**—A Pyrex diaphragm gage was constructed of the type shown in Fig. 1 by flattening a thin blown bulb. Before the diaphragm had cooled, the hot end of a 1.5-mm. Pyrex rod was stuck to the diaphragm half-way between the center and a side. This was melted off about 5 mm. from the diaphragm and flattened on the end. A $^3/_8$-inch galvanometer mirror was attached to this rod with sealing wax. When the sealing wax was permitted to spread over a large part of the mirror,

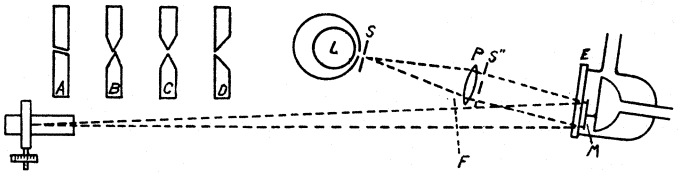


Fig. 1.

it warped the mirror on cooling. Therefore, care had to be taken to use as little sealing wax as possible. The diaphragm was 1 cm. in diameter and withstood one atmosphere pressure in either direction. It was found to have a sensitivity of 0.018 mm. of mercury per 0.01 mm. deflection at 3 meters. The average observational error in reading the pressure then was 0.006 mm. pressure. Another gage was constructed which withstood 10 cm. pressure. The average observational error for it was 0.00044 mm. pressure.

When a still more sensitive gage was constructed with an average observational error of 0.0002 mm. pressure, the mirror vibrated continuously, giving a band of light about 2 mm. wide in the eyepiece. This difficulty was overcome by placing the mirror M almost in contact with the plate glass E. This completely damped the oscillations of the mirror when the pressure was about atmospheric, but it vibrated when evacuated. This gage could only be used for measuring small changes of pressure. It had to be calibrated with a light liquid manometer instead of a McLeod gage.

In order to be certain that the gage had not moved before reading the pressure, a second mirror was attached to a rigid arm directly below the mirror on the diaphragm. The light from the double slits fell on both mirrors. The latter were adjusted until the two sets of interference bands fell in the field of view of the eyepiece. Thus one could check the "zero"

point at any time by taking the reading of the position of the interference bands from the fixed mirror. As a reference point, it was found to be almost as convenient to use the interference bands reflected from the surface of the plate glass covering the gage. However, they were less intense than those reflected from the silvered mirror. If the gage cannot be mounted rigidly in a fixed position, two mirrors may be attached to opposite sides of the diaphragm so that they rotate in opposite directions. If the mirrors are so attached that the line joining the centers of the mirrors is perpendicular to the line joining the points of attachment to the diaphragm, then one optical system will do for both mirrors. The pressure, then, may be measured in terms of the distance between the two sets of interference bands.

## Summary and Conclusions

A very simple optical system was constructed, by means of which it was possible to measure deflections of a three-meter optical lever with an average error of about 0.003 mm. An all-glass optical lever pressure gage was constructed. It had an average observational error of 0.006 mm. pressure and withstood an atmosphere pressure in either direction. A much more delicate gage had an average observational error of 0.0002 mm. pressure.

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[CONTRIBUTION FROM THE RICE INSTITUTE, HOUSTON, TEXAS]

# THE PREPARATION OF NEPHELOMETRIC TEST SOLUTIONS

BY ARTHUR F. SCOTT AND JOHN L. MOILLIET

RECEIVED OCTOBER 10, 1931 PUBLISHED JANUARY 7, 1932

The nephelometer, devised by Richards[1] and now employed in many atomic weight determinations, serves to compare the light reflected by two silver halide suspensions. These suspensions are formed in measured samples of the supernatant analytical solution, which is saturated with respect to the silver halide, by the addition of a known excess of silver ion in one case and an equivalent amount of the halide ion in the other. That the chief source of error in these nephelometric measurements resides in the preparation of the suspensions was fully recognized by Richards,[2] who laid great stress on the necessity of precipitating the two suspensions under conditions as nearly identical as possible.

No systematic study[3] has been made of the effect on the reproducibility

[1] Richards, *Proc. Am. Acad. Arts Sci.*, **30**, 385 (1894); Richards and Wells, *Am. Chem. J.*, **31**, 235 (1904); THIS JOURNAL, **27**, 502 (1905).

[2] Richards, *Am. Chem. J.*, **35**, 511 (1906).

[3] See P. V. Wells, "The Present Status of Turbidity Measurements," *Chem. Reviews*, **3**, 331 (1927).

of these suspensions of the many factors involved in their preparation. However, since the rate of addition of the precipitant and the manner of mixing it with the saturated solution would influence the number of particles formed in the suspension, it is conceivable that many of the irregularities met with in nephelometric observations are due to slight variations in one or both of these conditions.[4] A number of experiments which bear out this viewpoint will be described briefly in this note.

A saturated solution of pure silver chloride was prepared as follows. A dilute solution of pure silver nitrate was added slowly to a dilute solution of pure hydrochloric acid. After the resulting precipitate had been washed repeatedly with twice distilled water to remove the excess chloride, it was allowed to stand in a solution of 0.5 *M* nitric acid. Frequent shakings over a period of time were considered sufficient to saturate the acid solution. The above operations and all subsequent ones involving this solution were carried out in a dark room illuminated only by red light.

For precipitating the suspensions standard solutions were made up in the usual way. The silver solution contained 1.00 mg. of silver per ml. and the chloride solution contained an equivalent amount of chloride ion.

Nephelometric test solutions were prepared by mixing 20 ml. of the saturated solution and 2 ml. of the precipitant. Unless otherwise specified, samples of the first solution were always measured by means of a transfer pipet and those of the second from a buret. The precipitation of the suspensions in these test solutions was performed by three different methods which will be designated as pouring, stirring and instantaneous, and which are described briefly below.

**Pouring** (P).—The two solutions were measured out into separate nephelometer test-tubes. The saturated solution was then poured directly into the precipitant and the resulting solution was decanted back and forth between the two tubes to insure thorough mixing. This process apparently was first described by Stas.[4]

**Stirring** (S).—In this case the precipitant was added directly to the sample of the saturated solution and the two solutions were then mixed by stirring with a glass rod provided with a small glass ring at the lower end. This method was used by Richards, who considered it superior to that of Stas because it afforded more efficient mixing and also because it lessened the danger of contamination.

**Instantaneous** (I).—This third, new method was tried because it appeared to offer a means of obtaining a more uniform adddition of the

[4] Richards evidently considered this question, for he states [*Am. Chem. J.*, **31**, 239 (1904)]: "This procedure obviates any possible inconsistency arising from unequal speed of precipitation—a matter to be discussed in a subsequent paper." This paper, so far as the author can ascertain, was not published.

precipitant and also more rapid mixing of the two solutions. The device used is shown in Fig. 1. The outer tube was approximately 160 mm. × 28 mm.; the inner tube was 80 mm. × 10 mm. and was sealed together about 35 mm. from the top to form a small cup. Into the outer tube the sample of the saturated solution was delivered from a pipet. The cup, the top edge of which was above the surface of this solution, was filled with the precipitant, which was measured directly from a long-tipped buret. The drop of solution which adhered to the tip of the buret was readily removed on the bottom of the stopper. Then, with the ground-in glass stopper held firmly in place, the tube was quickly inverted and violently shaken for a short time. For comparison in the nephelometer the solution with the suspension was transferred, by pouring, to the usual nephelometer tube.

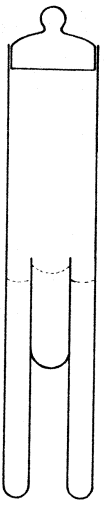

Fig. 1.

After a number of preliminary experiments involving the comparison of the suspensions prepared by the three different methods against suspensions of kieselguhr and barium sulfate as standards, the following procedure was adopted as the most satisfactory for our purpose. At one time three suspensions precipitated by one precipitant were prepared by each of the three methods. At fixed time intervals the three similar suspensions were compared with each other in the nephelometer and also one of them was compared with one suspension prepared by each of the other two methods. This procedure minimized the possibility of a serious error in the preparation of the sensitive suspensions and also eliminated any disturbing effects arising from a variation in temperature.

The turbidities of the suspensions prepared by the three methods, using silver or chloride ion as the precipitant, were consistently different. The general order of magnitude of the variations found is given below, the (I) turbidity being taken as a standard of reference:

| (I) | (P) | (S) |
|---|---|---|
| 1.0 | 1.4 | 1.6 |

These values represent the relative turbidities after the suspensions had been standing almost two hours. As a rule the turbidity of a suspension underwent very little change after the first hour.

The extreme variations in the turbidities of the different types of suspensions originate apparently in the speed with which the precipitant is added to the saturated solution rather than in the rate of mixing of the two solutions, for the latter factor is very much the same in the (I) and (P) methods. Indeed, the relative turbidities reflect roughly the relative speeds of adding the precipitant to the other solution, the more rapid rate resulting in the weaker turbidity. This conclusion would indicate

that the rate of mixing is a subordinate factor in determining the turbidity of a suspension.[5]

Originally it was hoped that the procedure adopted would furnish some information regarding the reproducibility of the turbidities obtainable by the different methods. Unfortunately, the data available are insufficient for a decisive answer to this question. In general, however, the order of decreasing reproducibility was, for both precipitants (P)—(S)—(I). This result is understandable in terms of our previous conclusion because in the (I) method a slight variation in technique would result in a relatively large change in the rate of adding the precipitant and thus would cause a large percentage change in the turbidity of the suspensions. The intermediate position of the (S) method is also understandable on the same ground when it is noted that, although considerable care was taken to insure uniform stirring, no particular attention was paid to the rate of delivery of the precipitant from the buret. At the conclusion of the investigation, to see whether the rate of addition in the case of the (S) method could affect the turbidity of the resulting suspension, the following experiments were tried. Three suspensions were prepared at one time by adding the precipitant from a pipet (A) as rapidly as possible, (B) dropwise with moderate rapidity, and (C) dropwise, very slowly. In each case the solution was promptly stirred after all the precipitant was added. The relative turbidities, using that of (A) as a basis, were:

| Precipitant | (A) | (B) | (C) |
|---|---|---|---|
| Chloride | 1.0 | 1.2 | 1.2 |
| Silver | 1.0 | 1.4 | 1.4 |

From these data it is quite obvious that a serious variation in the turbidity of a suspension can be induced by too rapid addition of the precipitant. On the other hand, when the rate of addition is fairly slow, there is a wide range in the speed of adding the precipitant, which results in the same turbidity.

Since the (S) method is the one commonly used in atomic weight investigations, the above results suggest the origin of many of the unaccountable inconsistencies which are found in making comparisons of the turbidities of the two suspensions, for the manner of adding the precipitant appears to be more significant than the stirring operation. Consequently, it is possible that a pipet would be superior to the customary buret because the rate of delivery of the standard solution can be controlled more readily.

[5] Kleinmann, *Biochem. Z.*, **99**, 149 (1919), studied the formation of silver chloride suspensions on the addition of sodium chloride solutions to a solution containing a slight excess of silver nitrate. Controlling the rate of addition of the precipitant and also the speed of stirring, he found the first factor was by far the more important in determining the turbidity of the resulting suspension. He likewise found that the more rapid addition of the precipitant resulted in a weaker turbidity.

Otherwise, according to the present evidence the (P) method is to be preferred.

The foregoing tests were made with a saturated solution of silver chloride which differed in one essential respect from the solutions examined in atomic weight investigations. In the latter case the saturated solution always contains, in addition to nitric acid, an extra ion introduced by the hydrolysis of the halide sample being analyzed. To determine whether this extra ion would modify in any way the results obtained with the acid solution, a new series of experiments was carried out with a saturated solution of silver chloride which was 0.5 *M* with respect to cadmium nitrate and also 0.1 *M* with respect to nitric acid. Only one divergence in the general results was noticed. When the precipitant was the chloride ion, the sequence of decreasing reproducibility of turbidities by the various methods was clearly (I)—(S)—(P).

This reversal in sequence is so marked as to be noteworthy. As a possible basis for its explanation it is allowable to suggest the phenomenon of adsorption. In the first place the apparent abnormality occurred only in the case of the negatively charged sol which can adsorb the positive cadmium ion. In the second place it is known[3] that adsorbed material can inhibit or "poison" the growth of precipitated nuclei. Indeed, some evidence of this effect has already been noted in atomic weight investigations. Thus, Hönigschmid and Birkenbach[6] in their analysis of bismuth trichloride found that the suspension precipitated with silver developed much more rapidly than that precipitated by chloride. Again in the study of the Ag:Br ratio Hönigschmid and Zintl[7] observed a decided difference in the rate of precipitation of the two suspensions. In this case the solution tested contained both arsenious and arsenic acids.

If adsorption is involved, as we have supposed, in the formation of a suspension and therefore in its ultimate turbidity, one consequence can be pointed out. Since the effect of adsorption can influence only one suspension, it may act under certain conditions to accentuate irregularities in the rate of adding the precipitant, especially if the nephelometric comparison is made after an arbitrary period of time. The effect in question would depend primarily on the specific nature of the extra ion. In this phenomenon of adsorption we have, therefore, another factor which contributes to the well-known sensitiveness of nephelometric suspensions to the conditions attending their preparation. In conclusion it may be suggested that in some cases one of the three methods of adding the precipitant may be decidedly superior. Each case, however, would have to be examined individually.

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[6] Hönigschmid and Birkenbach, *Ber.*, **54B**, 1873 (1921).

[7] Hönigschmid and Zintl, *Ann.*, **433**, 224 (1923).

## NOTE

**Note on the Potential of the Lead Electrode.**—In a recent communication[1] Randall and Cann describe a determination of the potential of the lead electrode from electromotive force measurements on the cell, Pb (in satd. amal.), $Pb(NO_3)_2$ (aq.) | $KNO_3$ (aq.) | KCl (aq.), AgCl (s), Ag (s), in which the electrolytes were flowed over the silver chloride and lead amalgam electrodes.

In an accompanying paper[2] the writer has demonstrated that the potential of the silver chloride electrode so designed is approximately 0.006 volt positive to a silver chloride electrode at equilibrium with the cell solution. On the other hand, laboratory data which the writer obtained several years ago indicate that the lead amalgam electrode practically attains its equilibrium potential instantaneously. It would seem, therefore, that the value of the potential of the lead electrode obtained by Randall and Cann (0.1203) involves an error of approximately 0.006 volt, the difference between the flowing and the equilibrium silver chloride electrode. By applying this correction, one approximates the value 0.1263 obtained by the writer[3] from measurements on the cell Pb (satd. amal.), PbCl (aq), AgCl (s), Ag (s).

There seems to be no necessity for washing the potassium chloride solution over the silver chloride electrode in the cell used by Randall and Cann. The flowing liquid junction could have been maintained just as well by introducing the potassium chloride solution in the arm between the electrode and the liquid junction bulb.

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PUBLISHED JANUARY 7, 1932

[1] Randall and Cann, THIS JOURNAL, **52**, 589 (1930).

[2] Carmody, *ibid.*, **54**, 188 (1932).

[3] Carmody, *ibid.*, **51**, 2905 (1929).

[CONTRIBUTION FROM THE FLEISCHMANN LABORATORIES]

# VEGETABLE AMYLASES. STUDY OF DIASTASE ACTION IN THE ABSENCE OF MALTOSE

BY ALFRED S. SCHULTZ AND QUICK LANDIS

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## Foreword

Studies of the kinetics of enzyme action have been but rarely made in the absence of end products. Determinations of the course of the reaction in most previous studies of diastatic activity have been made either (1) by noting the rate of degradation of starch as in the method of Wohlgemuth[1] utilizing the change in iodine reaction or (2) by observing the rate of appearance of maltose, usually by copper reduction.[2] Nearly every investigator has attempted to show that his results follow the usual monomolecular reaction formula, with but varying success. Brown and Glendinning[3] as well as Luers and Wasmund[4] definitely state that the earlier portion of their curve would not fit a first order reaction and the monomolecular velocity constants calculated by other investigators[5] all tend to rise during the reaction. Others[6] who worked with relatively concentrated enzyme solutions are the only ones who report results which follow at all closely this law.

**Kinetics in Absence of Maltose.**—In the present investigation the determination of sugars formed in the reaction by the usual tedious procedure has been replaced by a method much more convenient. Yeast is added to the reacting solutions in sufficient quantity to ferment out the sugars as rapidly as they are formed and the carbon dioxide evolved is collected and measured at frequent intervals (Fig. 1). The results obtained in comparison with the more usual methods are shown in Fig. 2 and Fig. 3. The linear character of the action in this case is obvious and the inhibition caused by added maltose (reported also by Wohl and Glimm)[7] is quite apparent. As far as can be learned this is the first example of an enzyme reaction for which conditions have been found under which the velocity appears to be independent of the time over such a large portion of the reaction.[7a] If an explanation were to be offered for the apparent simplicity

[1] Wohlgemuth, *Biochem. Z.*, **9**, 1 (1910).

[2] Pollack, *Wochschr. Brau.*, **20**, 595 (1903).

[3] Brown and Glendinning, *J. Chem. Soc.*, **81**, 388 (1902).

[4] H. Luers and W. Wasmund, *Fermentforschung*, **5**, 169 (1922).

[5] Euler and Svanberg, *Z. physiol. Chem.*, **112**, 193 (1921).

[6] Luers in Carl Oppenheimer's "Die Fermente und ihre Wirkungen," **1928**, 5th ed. Vol. III, p. 883; Willstätter, Waldschmidt-Leitz and Hesse, *Z. physiol. Chem.*, **142**, 14 (1925).

[7] A. Wohl and E. Glimm, *Biochem. Z.*, **27**, 349 (1910).

[7a] P. Rona and R. Ammon [*ibid.*, 181 (1927)] report that lipase activity does not vary when the $P_H$ is kept constant by titration.

of this action it would seem logical to conclude that all inhibiting factors, including reversible combination with end products, appear to be eliminated. The results also seem to substantiate the Michaelis[8] theory and the velocity of the reaction as measured is that of the decomposition of the enzyme–substrate complex, the concentration of which remains essentially constant as long as a sufficient excess of substrate is present.

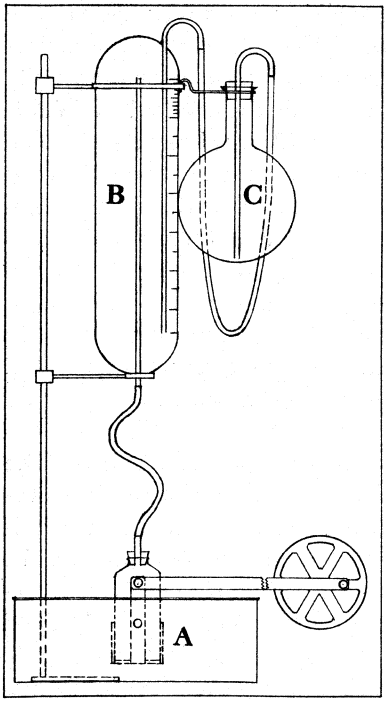


Fig. 1.—Apparatus: A, cradle in thermostat carrying six bottle clamps; B, 1-liter fermentometer; C, 1-liter flask as leveling bulb.

Fermentation of the products of the acid hydrolysis of the starch used gave 1250–1300 cc. of gas per 125 cc. of 5% solution. In our tests with the products of enzyme hydrolysis 950–1000 cc. was obtained. This corresponds to the usual 75% conversion and corroborates the residual dextrin theory.

**Inactivation of Enzyme.**—Among the factors which may be considered to explain any falling off in the initial rate[9] may be listed, (1) reversible combination of the products (mentioned above) with the enzyme, (2) insufficient saturation of enzyme by substrate, (3) irreversible destruction of the enzyme by heat, adsorption, etc. In the progress of this investigation it was found that shaking, particularly in the case of malt diastase, caused a serious diminution in activity as shown in Fig. 4, curves 1 and 2, quite similar to the effect of adsorbents such as diatomaceous earth or filter paper pulp (Fig. 4, curves 4 and 6, and Fig. 5, curves 3 and 6). The addition of small amounts of gelatin, saponin, albumin, casein and peptone, however, enabled each enzyme to act linearly (Fig. 4, curves 3, 5 and 7, and Fig. 5, curves 2 and 4), but if added after inactivation did not restore the activity. It should be noted, however, that soy diastase produces this type of reaction without the presence of any added protective agency. The inhibition is not oxidative for the presence of inert gases is without effect. Glycine and agar were found to be without action.

In explanation of the effect of shaking we may call attention to the work

[8] L. Michaelis and M. L. Menten, *Biochem. Z.*, **49**, 333 (1913).

[9] Haldane, "Enzymes," Biochemical Monographs, Longmans, Green and Co., London, **1930**, p. 92.

of Ramsden,[10] who found that shaking of protein solution caused a precipitation or "de-solution" of the solute by agglomeration of the viscous coatings formed on the free surfaces of the solution. It is highly probable that the enzyme is removed from the reaction in this way. Others[11] in studying the inactivation of enzymes by shaking found that the presence of small amounts of saponin and certain proteins prevented the inactivation and explained it on the basis of surface tension, *i. e.*, saponin, producing a lower surface energy than the enzyme, forced the latter away

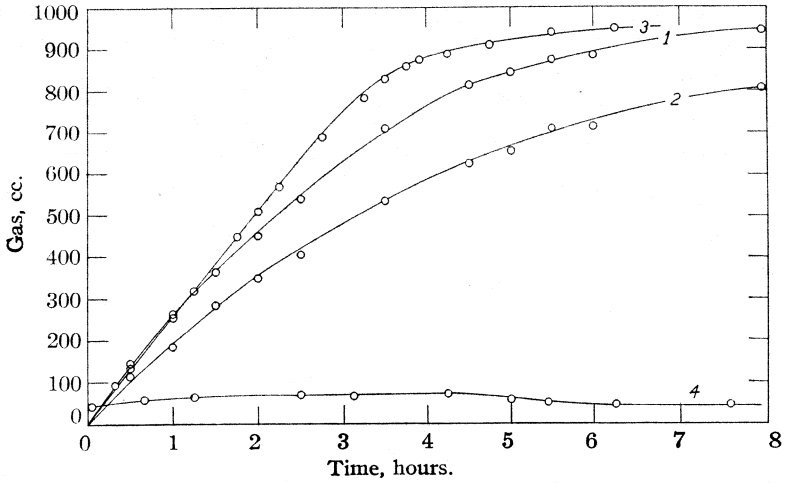


Fig. 2.—Malt diastase: effect of end-products on activity. Reacting solutions contained 125 cc. of 5% soluble starch solution, citrate buffer, 0.030 g. of malt sirup, 0.03 g. of saponin; total volume 146 cc., and (1) no added maltose, no yeast; sugars by copper reduction, calculated to equivalent gas. (2) Five per cent. added maltose, no yeast; sugars by copper reduction, calculated to equivalent gas. (3) No maltose, 5 g. of yeast, gas measured. (4) Residual reducing substances in (3) by copper reduction, calculated to equivalent gas.

from the surface, or competed more strongly for positions in the surface layer. We are led to consider the same explanation in the case of inactivation by adsorbents, *i. e.*, competition for positions on the adsorbing surface. In passing it might be mentioned that it does not seem that Przylecki's explanation of inactivation by adsorption[12] is substantiated, since the falling off in the velocity occurs even in the presence of excess

[10] W. Ramsden, *Proc. Roy. Soc.* (London), **72,** 156 (1904).

[11] A. and S. Schmidt-Nielson, *Z. physiol. Chem.*, **68,** 317 (1910); E. Abderhalden and W. Guggenheim, *ibid.*, **54,** 331 (1907); M. M. Harlow and P. G. Stiles, *J. Biol. Chem.*, **6,** 359 (1909); A. O. Shaklee and S. J. Meltzer, *Am. J. Physiol.*, **225,** 81 (1909); H. C. Bradley, *J. Biol. Chem.*, **6,** 133 (1909).

[12] S. J. Przylecki and co-workers, *Biochem. J.*, **21,** 1025 (1927).

starch when the enzyme is adsorbed, although this difference may be due to $P_H$.

**Concentration Effects.**—Eadie[13] has shown that diastatic activity is practically proportional to enzyme concentration. In the case of soy diastase, Fig. 6, the enzyme concentration of curve 2 is two and one-half times that of curve 1 and the rate is within the limits of error two and one-half times as great. Variations of substrate concentration, Fig. 7, are more important as from them we may calculate the value of the Michaelis constant. This constant $K_m$ for a flour diastase, calculated from the data

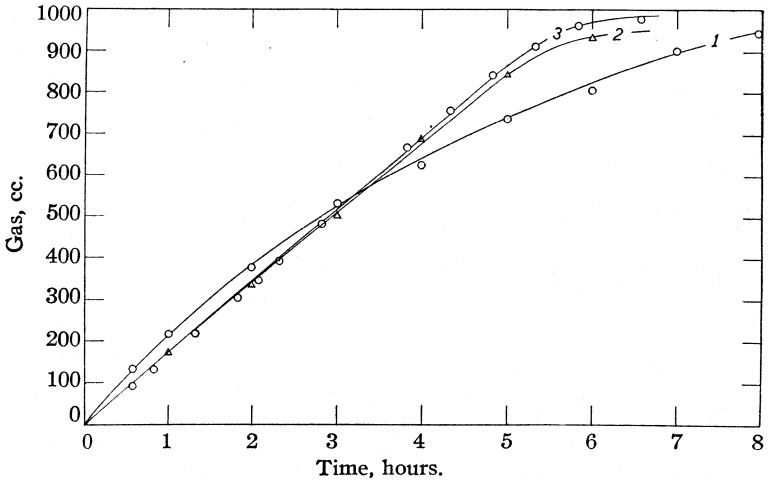


Fig. 3.—Soy diastase: effect of end-products on activity. Reacting solutions contained 125 cc. of 5% soluble starch solution, citrate buffer, 0.05 g. of ground soy bean, no saponin; total volume 135 cc., and (1) no added maltose, no yeast, drop in polarization calculated to equivalent gas. (2) Same, with 5 g. of yeast; drop in polarization calculated to equivalent gas. (3) Same, with 5 g. of yeast, gas measured.

presented in Fig. 7, is about 0.25 in units of per cent. starch. K. Sjoberg and E. Ericksson[14] have found $K_m$s 0.4 and 0.5 for malt amylase. It is believed that the results of this investigation substantiate further the Michaelis theory and the idea that the kinetics of enzyme action is fundamentally simple; the difficulty arises in sorting out the various inhibitions to which these labile substances are subject.

## Experimental Procedure

**Principle.**—The basis of the method is the removal of the reaction product, maltose, as rapidly as it is formed in the reaction by fermentation

[13] G. S. Eadie, *Biochem. J.*, **20**, 1016 (1926).

[14] K. Sjöberg and E. Eriksson, *Z. physiol. Chem.*, **139**, 118 (1924).

with a sufficiently large quantity of yeast. A quantity of gas, carbon dioxide, is formed, collected and periodically measured, which is stoichiometrically related to the amount of sugar produced (under actual conditions 1 g. of maltose is equivalent to 220 cc. of carbon dioxide at 25° and 1 atm. pressure). Supersaturation of the reacting solution with carbon

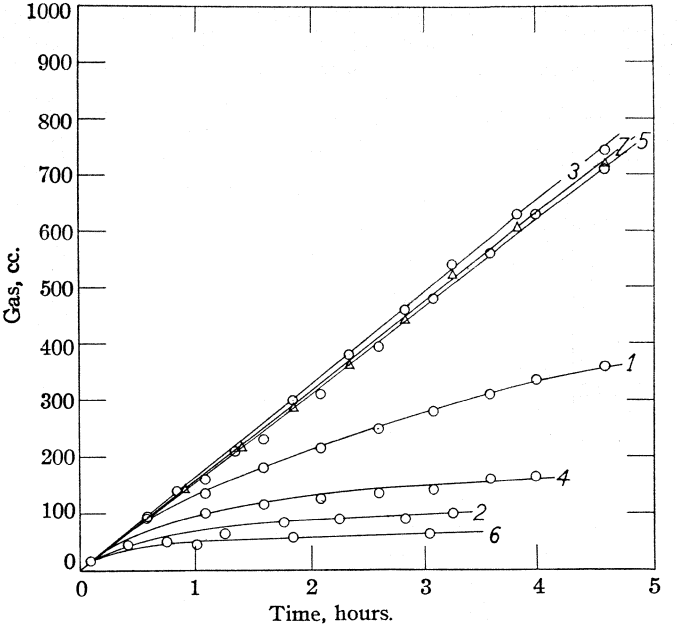


Fig. 4.—Malt diastase: effect of certain protective and destructive agencies on activity. Reacting solutions contained 125 cc. of 4.5% soluble starch solution, citrate buffer, 0.015 g. of malt sirup, 5 g. yeast; total volume 146 cc. and (1) nothing (or 0.5 g. of glycine or 0.5 g. agar). (2) Nothing (enzyme from a 1% solution of the malt sirup shaken two hours previous to test). (3) 0.5 g. of gelatin (or 0.03 g. of saponin, 0.5 g. of albumin, 0.5 g. of casein or 0.5 g. of peptone). (4) 1.0 g. of filter paper pulp. (5) 1.0 g. of filter paper pump plus 0.5 g. of gelatin. (6) 1.0 g. of diatomaceous earth. (7) 1.0 g. of diatomaceous earth plus 0.5 g. of gelatin.

dioxide is prevented by constantly shaking the mixture. It has been found necessary to "acclimatize" the yeast to the fermentation of maltose at large rates in order to prevent a short lag period at the beginning of enzyme action, and this as well as a preliminary saturation of the reacting solution with carbon dioxide is accomplished by an initial dosage of maltose before the addition of the enzyme. The changes due to the internal metabolic functions of the relatively small quantity of yeast used were found to be negligible in comparison with other experimental errors.

**Apparatus.**—Figure 1. Six 200-cc. wide-mouthed reaction bottles are attached by means of spring fastening clamps to a cradle of strap iron. The cradle is continuously rocked through an arc of about 20° in an electrically controlled thermostat by a small motor at a rate of about 120 oscillations per minute. Six 1-liter gasometers or gas burets are attached by flexible connections to their respective bottles. The water expelled by the evolved carbon dioxide is collected in liter wash bottles which also serve as leveling bulbs when taking readings. A layer of kerosene serves to minimize solution of carbon dioxide in the water. While such a layer is not completely impervious to the gas, it was found in a blank experiment that the rate of solution was negligible in comparison with that of the activity being measured.

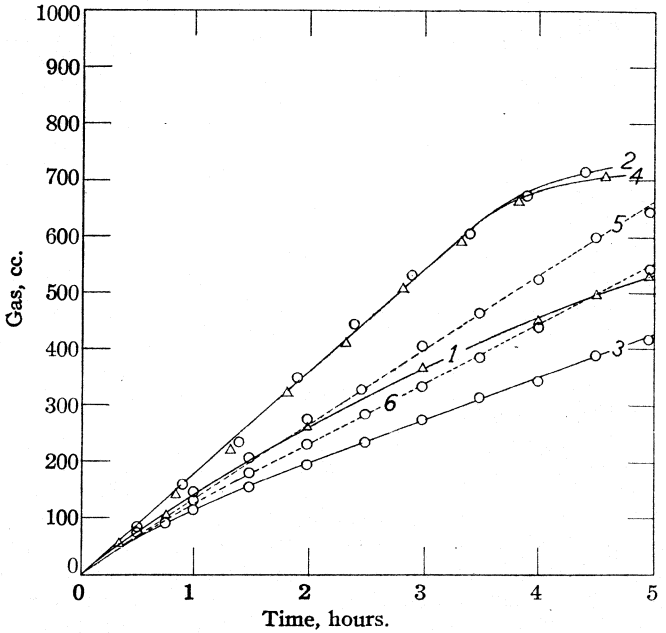


Fig. 5.—Wheat flour and ground soy bean diastase: effect of certain protective and destructive agencies on activity. Reacting solutions contained 125 cc. of 5% soluble starch solution, citrate buffer, 5 g. of yeast; total volume 146 cc., and (1) 0.035 g. of flour only. (2) Same, plus 0.5 g. of gelatin. (3) 0.035 g. of flour plus 1.0 g. of diatomaceous earth. (4) Same, plus 0.5 g. of gelatin. (5) 0.035 g. of ground soy bean only. (6) Same, plus 1.0 g. of diatomaceous earth.

**Reagents.**—A suitable unbuffered soluble starch solution of about 5 or 6% solids such as that prepared by the prolonged action of hydrochloric acid in the cold in commercial potato starch was used.[15] A buffer solution of 100 g. of potassium citrate, 20 g. of citric acid and 20 g. of primary ammonium phosphate per liter, sterilized by boiling, has been found satisfactory as it gives very closely the optimum $P_H$, 4.5 to 5.5. A quantity of fresh bakers' yeast, or any yeast of similar fermenting strength, and pure maltose complete the list of reagents.

[15] H. C. Gore, THIS JOURNAL, 47, 281 (1925).

**Procedure.**—This general procedure was followed rather closely for most of the experiments reported herein. Five grams of fresh pressed yeast, 1 to 2 g. of maltose, 125 cc. of starch solution, 15 cc. of buffer solution and 3 cc. of 1% saponin solution or any other material, the action of which is to be tested, are placed in the reaction bottle in the cradle and the bottle is connected to the gasometer. Shaking is continued until the maltose is completely fermented (usually about two hours). The shaking is then stopped, the gasometers reset to zero, a definite volume of the aqueous solution or suspension of the diastatic material (1%) added and the time of addition noted. Shaking is resumed and continued until the test is finished, except for the short intervals during

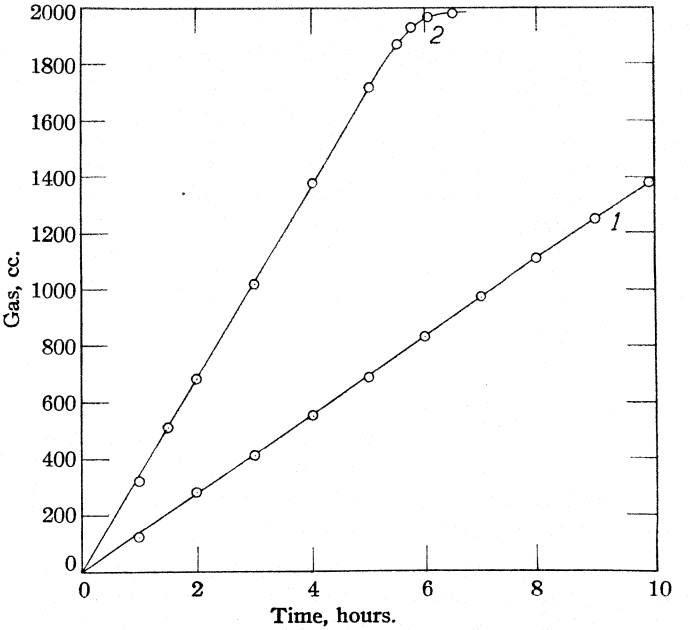


Fig. 6.—Soy bean diastase: effect of variations in enzyme concentration. Reacting solutions contained 270 cc. of soluble starch solution, citrate buffer, 10 g. of yeast; total volume 310 cc., and (1) 0.04 g. of ground soy bean. (2) 0.10 g. of ground soy bean.

which readings of the volume of gas are taken. These readings can be made conveniently at quarter or half hour intervals. It is desirable, although not absolutely necessary, to work in a constant temperature room; at any rate the fluctuations in room temperature should be kept to a minimum. For strictly comparable work barometer variations should also be taken into consideration. The thermostat was maintained at a temperature of 30 ± 0.2° in this investigation. A typical set of data is given in Table I, which shows the effect of gelatin in the preparation of the diastatic extract. The agreement with other methods is close, as is shown in Fig. 3, curves 2 and 3, in which the rate of degradation of starch was followed polariscopically in a parallel experiment. The experimental points are calculated from the ratio of cc. of gas to degrees Ventzke, equal to 17.4 cc. per degree; for curve 1 (maltose present) the ratio is 61.4.

The Lintner value readily can be calculated from the data thus obtained by substituting in the formula $°L. = fv/tw$. In this expression $v$ is the

TABLE I

QUANTITIES OF MATERIALS USED IN EACH EXPERIMENT

Maltose, 1 g.; buffer, 15, cc.; starch soln., 125 cc.; yeast, 5 g.; gelatin, 0.5 g.

After sugar was fermented enzymes added as follows:

| Expt. | cc. | G. | |
|---|---|---|---|
| 1 | 3.5 | 0.035 | 1 g. Flour + 0.5 g. gelatin in 100 cc. |
| 2 | 3.5 | .035 | 1 g. Flour, no gelatin in 100 cc. |
| 3 | 6.0 | .06 | 1 g. Ground malt + 0.5 g. gelatin in 100 cc. |
| 4 | 6.0 | .06 | 1 g. Ground malt, no gelatin in 100 cc. |
| 5 | 1.5 | .015 | 5 g. Malt sirup + 0.5 g. gelatin in 500 cc. |
| 6 | 1.5 | .015 | 5 g. Malt sirup, no gelatin in 500 cc. |

GAS EVOLVED AT TIMES INDICATED, CC.

| Start..... 11:20 / Time | 11:20 1 | 11:20 2 | 11:20 3 | 11:21 4 | 11:21 5 | 11:21 6 |
|---|---|---|---|---|---|---|
| 12:15 | 135 | 100 | 135 | 130 | 135 | 120 |
| 12:45 | 225 | 165 | 230 | 220 | 220 | 200 |
| 1:15 | 300 | 230 | 310 | 305 | 290 | 280 |
| 1:45 | 395 | 300 | 405 | 400 | 370 | 365 |
| 2:15 | 480 | 370 | 500 | 490 | 450 | 450 |
| 3:35 | 700 | 550 | 740 | 730 | 660 | 670 |
| 3:50 | 745 | 600 | 790 | 780 | 705 | 715 |
| 4:00 | 760 | 610 | 820 | 815 | 730 | 740 |
| 4:30 | 825 | 680 | 890 | 885 | 810 | 815 |
| 5:25 | 940 | 815 | 1000 | 995 | 940 | 940 |

volume of gas in cc. produced in $t$ hours by $w$ g. of diastatic material during the linear portion of the curve and $f$ a conversion factor. For °L. equivalent to that determined polariscopically at 20°,[15] $f = 0.038$, the gas being determined by exact adherence to the procedure described above. If the factor weight of 0.038 g. of enzyme is used, the cc. per hour will be directly the °L. of the material. The temperature coefficient for the soy, wheat flour and malt diastases has been found to be about 1.9 per 10° between 20 and 30°, in agreement with the results of previous investigations. As reported also by Ford and Guthrie,[16] it has been found that in the preparation of the aqueous suspension of flour a small amount of protective substance such as 0.5 g. of gelatin per 100 cc. of 1% suspension of diastatic material should be present in order to obtain the maximum value of diastatic activity.

**Precautions.**—The necessity of having the yeast in an acclimatized state and the solution saturated with carbon dioxide before beginning an experiment has been mentioned. In addition it is necessary to adjust the enzyme concentration or the amount of yeast added so that the latter is never fermenting at its maximum rate, *i. e.*, the yeast must keep ahead of the enzyme. The "threshold value" of sugar or reducing substances which apparently is required for active fermentation is indicated in Fig. 2, curve 4. In actual determinations of diastatic power the addition of 0.03 g. of saponin or 0.5 g. of gelatin to the reacting mixture is necessary

[16] Ford and Guthrie, *J. Inst. Brew.*, **14**, 61 (1908).

to prevent adsorption at the surface. It should be noted that the filtration of any diastatic solution[17] is extremely likely to decrease its activity (Fig. 4, curve 4).

**Limitations.**—Experiments are limited to amylases which are active in the $P_H$ range in which active fermentation occurs, *viz.*, 4.0 to 6.0. The fermentation rate also limits the ratio of enzyme to substrate concentrations which can be studied. When small concentrations of starch are involved (Fig. 7, 0.168% starch) it becomes necessary to substitute a 100-cc.

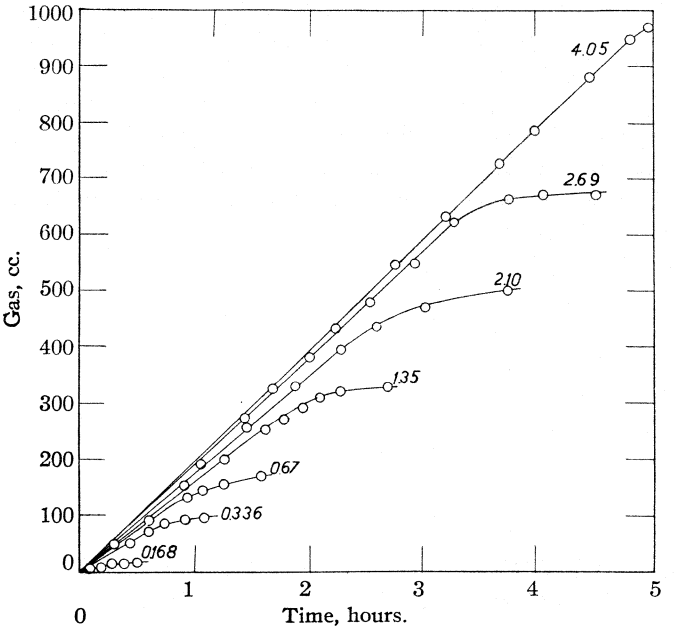


Fig. 7.—Wheat flour diastase: effect of variations in substrate concentration. Reacting solutions contained citrate buffer, 0.01 g. of saponin, 0.038 g. of flour, 5 g. of yeast; total volume 140 cc. and the percentages of soluble starch (dry basis) indicated by the figures.

gas buret for the one-liter fermentometer. In addition it is necessary to add the enzyme by a Victor Meyer capsule or similar device after the initial maltose has been fermented out to guard against change in concentration of carbon dioxide in the vapor phase. Smaller amounts of carbon dioxide formed may be measured by weighing in soda lime tubes. The principle of this method would lend itself to the investigation of invertase or maltase activity by the use of the proper invertase or maltase free yeast.

[17] D. J. Levy, Abstract 3091, Walton, "Comprehensive Survey of Starch Chemistry."

## Summary

In the description of this investigation the following points have been presented.

1. Diastatic action of certain vegetable amylases in the absence of inhibitive agencies such as maltose, irreversible adsorption on interfaces due to shaking or on diatomaceous earth or filter paper pulp, is found to be a linear function of time and enzyme concentration throughout large variations in substrate concentration.

2. Adsorptive agents such as extended liquid–vapor surface films caused by continued shaking, diatomaceous earth or filter paper pulp are found to have marked inhibitive effects. The initial presence of small amounts of saponin, gelatin, albumin, casein or peptone, however, prevents this inhibition. Glycine and agar are found to be without effect.

3. Unpurified, ground soy bean diastase does not appear to be subject to adsorption at extended liquid–vapor surface films caused by shaking. Wheat flour and malt sirup enzymes, however, are quite subject to this effect.

4. The Michaelis constant for a flour diastase has been found to be about 0.25 in terms of percentage substrate concentration.

5. A convenient method for the study or determination of diastatic activity is described in which the sugars are fermented out by yeast as rapidly as formed, and the resulting carbon dioxide collected and measured at frequent intervals.


NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

# THE CHEMICAL COMPOSITION OF OIL OF RUVETTUS PRETIOSUS, THE "CASTOR OIL FISH"[1,2]

BY WARREN M. COX, JR., AND E. EMMET REID

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*Ruvettus pretiosus* was described ichthyologically by Cantraine[3] in 1837 and by Lowe[4] in 1841. The latter author reports, "it is affirmed that the bones abound in an oil or marrow, which, when they are sucked incautiously, produces diarrhea." Since this initial observation various in-

[1] The material in this article is extracted from a thesis submitted by Warren M. Cox, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

[2] Presented to the American Chemical Society at its meeting in Atlanta, Georgia, April, 1930.

[3] F. J. Cantraine, "Memoire sur un Poisson nouveau (*Ruvettus temminckii*) trouvé dans le Canal de Messine, etc." Nouveaux Memoires Academie Royale Sciences et Belles Lettres, Bruxelles **1837**, Vol. 10, 1–2.

[4] Richard T. Lowe, "A Synopsis of the Fishes of Madeira, etc.," *Trans. Zoölogical Society*, London, 2, 180–181 (1841).

vestigators[5,6,7,8] have extended and confirmed this observation as to the purgative qualities of the oil. The oil from the flesh of the fish is as remarkable in this effect as is the smaller amount obtainable from the bones. Gudger[9] has compiled the available information on this species and on the purgative qualities of its oil. C. B. Nordhoff[10] has recently said, however, that undoubtedly the purgative quality of the oil has been over-emphasized.

It was therefore deemed of interest[11] to undertake a chemical study of the oil with the view of isolating and identifying the purgative principle or principles, if any. Two quarts of the oil were obtained through the kindness of Dr. E. W. Gudger of the American Museum of Natural History and Mr. Donald G. Kennedy, Vaitupu, Ellice Islands, South Seas. The pharmacological evaluation of the "purgativeness" of the oil and its components has been done by Dr. David I. Macht and Dr. Maria J. Barba-Gosé. Their results on the principal constituents of the oil, expressed in arbitrary relative units, are given in Table II. The technique employed by them in determining these values has been published elsewhere.[12]

The chemical analysis of the oil shows it to consist of about equal proportions of saponifiable and unsaponifiable constituents. These are, respectively, fatty acids and normal, straight chain alcohols. The absence of an appreciable amount of glycerol leads to the conclusion that the oil consists primarily of esters of the type, cetyl oleate and oleyl oleate. This conclusion is further warranted by the absence of appreciable amounts of free acid or alcohol, as indicated by the nullity of the acid value, and the fact that the hydroxy acid identified accounts for the acetyl value.[14a] On the basis of 1 kg. of oil, 1.78 mols of fatty acids and 1.28 mols of alcohols have been identified. Since the mols of acid are greater than those of alcohol, a considerable part of the unidentified unsaponifiable matter must have been alcohols of higher molecular weight. The individual constituents which have been identified, with the percentages present, are given in the following table.

[5] Louis Becke, "By Rock and Pool on an Austral Shore," London, **1901**, pp. 63 and 148–158.

[6] Augustin Krämer, "Der Purgierfisch der Gilbertinseln," Globus, **1901**, Vol. 79, pp. 181–183.

[7] Max Weber, "Siboga Expeditie, Monographie I. Introduction et Description de l'Expedition," Leiden, **1902**, pp. 96–97.

[8] Frau A. Weber-van Bosse, "Ein Yahr am Bord I. M. S. Siboga," Leipzig, **1905**, pp. 243–244.

[9] E. W. Gudger, "A New Purgative, the Oil of the 'Castor Oil Fish,' Ruvettus," *Boston Med. Surg. J.*, **192**, 107–111 (1925).

[10] C. B. Nordhoff, *Natural History*, **28**, 40–45 (1928).

[11] We wish to acknowledge our indebtedness to Dr. E. W. Gudger and Dr. D. I. Macht for bringing this problem to our attention.

[12] D. I. Macht and Barba-Gosé, *J. Proc. Soc. Exptl. Biol. Med.*, **28**, 772–774 (1931).

TABLE I

THE COMPOSITION OF RUVETTUS OIL

| Ruvettus | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fatty Acids (54.4%) | | | | Unsaponifiable (48.5%) | | | |
| Unsaturated | 52% | Saturated | 1.5% | Unsaturated | 28.5 | Saturated | 18.5 |
| Palmitoleic | ? | Stearic | 1.5% | Oleyl alc. | 14.3 | Tetradecyl alc. | trace |
| Oleic | 40% | | | | | | |
| Gadoleic | 1.3 | | | Cholesterol | 0.15 | Cetyl alc. | 16.2 |
| Erucic | 0.3 | | | Squalene | trace | Octadecyl alc. | 2.1 |
| $C_{24}H_{46}O_2$ | trace | | | | | | |
| $C_{26}H_{50}O_2$ | trace | | | | | | |
| Hydroxyoleic | 7% (approx.) | | | | | Glycerol | trace |

The absence of any appreciable quantity of saturated acid, and especially the absence, in a fish oil, of more than traces of acids more highly unsaturated than oleic, together with the noteworthy completeness of the oleic acid series from $C_{16}$ to $C_{26}$, makes the oil of more than passing interest. The hydroxy oleic acid seems to be an isomer of ricinoleic acid, but possesses none of the chemical or pharmacological characteristics of this acid. The pharmacological evaluations of the principal components are given in the following table.

TABLE II

RELATIVE PURGATIVE ABILITY OF OILS AND FRACTIONS

| Sample | No. of Rats | "Purgativeness" |
|---|---|---|
| Emulsion carbon black | ... | 0 |
| Olive oil | 4 | 10 |
| Castor oil | 3 | 25 |
| Ruvettus oil | 7 | 23 |
| Ethyl oleate | 9 | 18 |
| Ethyl hydroxyoleate | 4 | 14 |
| Oleyl acetate | 7 | 29 |
| Cetyl acetate | 6 | 32 |

These results seem to indicate that the oil is in the castor oil class, the relatively large doses required for purgation indicating a mild laxative. It is also evident that no one constituent is responsible for this action, and that the effect of the combined constituents accounts for the action of the whole oil. Squalene had been reported[13] as having purgative action but it is present here only in traces. It is also to be noted that cetyl acetate has recently been fed in rather large amount in the course of a metabolism experiment[14] and no observation is reported as to an ensuing diarrhea. One of us (W. M. C.) ingested an ounce of the whole Ruvettus oil *per os* with no noticeable effects.

## Experimental

The two quarts of oil were of different color, one a very pale straw-yellow (I) and the other verging toward a light reddish-yellow (II). The first

[13] H. J. Channon, *Biochem. J.*, **20**, 400–408 (1926).

[14] R. Mancke, *Z. physiol. Chem.* (Hoppe-Seyler), **162**, 244 (1926–1927).

was obtained by boiling the flesh and skimming off the oil, and the second by roasting. Both were very pleasant smelling liquids with no suggestion of the fishy odor characteristic of highly unsaturated fish oils, and were wax-like solids at zero degrees with no definite solidification point. The physical characteristics are presented in Table III.

TABLE III

PHYSICAL CHARACTERISTICS OF RUVETTUS OIL[14a]

| | I | II |
|---|---|---|
| Density 25°/4° | 0.8697 | 0.8700 |
| Iodine no. (Wijs) | 83.9 | 74.4 |
| Saponification no. | 115.4 | 124.0 |
| Refractive index 25°/D | 1.4633 | 1.4628 |
| Acid value | 0 | 0 |
| Reichert-Meissl no. | 0 | 0 |

**Separation of the Saponifiable and Unsaponifiable Constituents.**—Exploratory work was done with oil I, while II was reserved for the final complete analysis. It was found in these preliminary experiments that the large amount of unsaponifiable substances present served to make their extraction extremely difficult, unless the correct ratio of water, alcohol and ether was used. The following procedure was adopted.

Two hundred gram batches of the oil were refluxed with 1000 cc. of 2 *N* alcoholic potash for thirty minutes. About 700 cc. of alcohol was distilled off and the soap poured into 2 liters of hot water in a 6-liter Florence flask. After cooling, 2 liters of ether were added, throughly shaken and the layers separated. Only about 1 liter of ether is separable here. This extraction was repeated three times with 1-liter portions of ether, the extracts combined, washed with water and the ether evaporated. The alkaline liquors were acidified and likewise extracted three times with 500-cc. portions of ether. On evaporation of these extracts the free fatty acids were obtained. Both fractions, the

TABLE IV

SEPARATION OF SAPONIFIABLE AND UNSAPONIFIABLE CONSTITUENTS

The iodine numbers were determined by the Wijs method.

| | Weight, | Unsaponifiable | | | Saponifiable | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Oil | g. | g. | % | I no. | g. | % | I no. | Neut. no. | Av. mol. wt. |
| I | 200 | 98.3 | 49.3 | 78.8 | 107.5 | 53.8 | 93.3 | 189.5 | 295.7 |
| | 150 | 75.5 | 50.3 | 79.0 | 82.3 | 54.8 | 92.3 | 188.0 | 298.4 |
| II | 200 | (81) | | 57.5 | 107.0 | 53.8 | 93.4 | 190.2 | 294.4 |
| | 200 | 94.0 | 47.0 | 58.5 | 110.0 | 55.0 | 92.6 | 187.6 | 299.1 |
| | 200 | 95.0 | 47.4 | 58.0 | 110.0 | 55.0 | 92.1 | 187.6 | 298.1 |
| Average | | | 48.5 | | | 54.4 | 92.7 | 188.6 | 297.1 |

[14a] At the end of the analysis it was thought necessary, in the light of the hydroxy acid and alcohols that had been identified, to determine the acetyl value. Only a small sample of oil (I) was available and this had become somewhat rancid, as an acid value of 6.3 would indicate. Its acetyl value was 11.4. Considered in conjunction with the increase in acid value, and the possible acetylation of small amounts of free alcohol and cholesterol, this does not exclude the possibility that some of the hydroxy acid was present as an inner anhydride.

saponifiable and unsaponifiable, were heated to 90–100° in a stream of carbon dioxide until all water had been removed. The data are given in Table IV.

The sum of these two fractions gives a percentage of 102.9, against a theoretical for oleyl oleate of 103.3. The iodine number and the neutralization number of the fatty acids are 92.7 and 188.6, respectively. This compares suggestively with the theoretical values of 90 and 198.9 for pure oleic acid.

**Analysis of the Saponifiable Fraction.**—The standard method for the separation of saturated and unsaturated fatty acids, the lead soap–ether method,[15] gave no saturated insoluble lead soap. By means of the Twitchell lead soap–alcohol procedure[16] no better result was obtained. Accordingly the free fatty acids were esterified and then fractionated at 5 mm.

Three hundred and twenty-one grams was dissolved in 320 cc. of ethyl alcohol containing 3.5% HCl by volume, 84 g. of calcium chloride (anhydrous) added, and refluxed for two days. After thorough washing there was but 0.2% free acid present. Fractionation was carried out in a small column.

TABLE V

FRACTIONATION OF ETHYL ESTERS OF THE SAPONIFIABLE FRACTION

| Fractions | to 180° | 180–190° | 190–195° | Residue |
|---|---|---|---|---|
| Weights | 11.3 | 125.8 | 140.4 | 65.2 |
| Percentage | 3.3 | 36.7 | 40.8 | 19.2 |
| Iodine no. | 77.2 | 81.3 | 82.2 | 88.3 |
| Saponification no. | 190.7 | 191.4 | 186.6 | 159.7 |
| Molecular wt. | 294 | 293 | 300.7 | 351.3 |

By applying the Twitchell lead soap–alcohol procedure to the lower-boiling fraction, 0.05 g. of an acid was obtained which melted at 74.5° and had a molecular weight of 293.3. The remainder was reësterified and redistilled. It boiled at 205–213 (15 mm.), had an iodine number of 82.3, $d_4^{25}$ 0.8665 and $n_D^{25}$ 1.4511. The calculated iodine number of ethyl oleate is 81.2 and the density is recorded[17] as $d_{25}$ 0.8671.

**Fractions 180–190° and 190–195°.**—These two fractions were combined and redistilled at 15 mm.

TABLE VI

REDISTILLATION OF ETHYL ESTERS

| | to 200° | 200–205° | 205–210° | 210–212° | 212° | Residue |
|---|---|---|---|---|---|---|
| Weights | 13.7 | 12.1 | 60.4 | 128.3 | 16 | 9.3 |
| Iodine nos. | 77.2 | 80.2 | 82.1 | 81.6 | 83.6 | 84.8 |
| Sapon. nos. | 186.2 | 183.5 | 183.4 | 184.2 | 179.5 | 171.6 |

The lows were combined with the first fraction of the previous distillation and treated as described there.

Oleic acid has been best purified by crystallization of its lithium salt. Moore,[18] Armstrong and Hilditch,[19] and Tsujimoto and Kimura[20] have proposed a certain tech-

[15] G. S. Jamieson, *J. Assoc. Off. Agri. Chem.*, **11**, 301 (1928); **12**, 44 (1929).

[16] E. J. Twitchell, *J. Ind. Eng. Chem.*, **13**, 806 (1921).

[17] E. Kröber, *Z. physik. Chem.*, **93**, 648 (1919).

[18] C. W. Moore, *J. Soc. Chem. Ind.*, **38**, 322T (1919).

[19] E. F. Armstrong and T. P. Hilditch, *ibid.*, **44**, 43T (1925).

[20] M. Tsujimoto and K. Kimura, *J. Chem. Ind.* (Japan), **26**, 891 (1923); **23**, 1007 (1920).

nique. It was found convenient to dissolve the free acid in 95% alcohol and neutralize it with aqueous lithium hydroxide solution of such a strength as to make the alcohol about 80%. The lithium salt crystallizes beautifully.

**Fraction 200–205°.**—The lithium salt–alcohol method gave two crops of crystals, the fatty acids from which had iodine numbers of 76.4 and 77.5, and molecular equivalents of 286.7 and 285.3, indicating the majority to be oleic acid, with some saturated acid present. The lithium soap soluble in alcohol was converted to the free acid and had a molecular equivalent of 275.3—suggesting palmitoleic acid.

**Fraction 205–210°.**—This fraction was treated as above; the constants of the fatty acids from the lithium salts agreed fairly well with those for oleic acid. When they were treated by the lead soap–alcohol method, 0.1 g. of insoluble lead salt was obtained. The free fatty acid had an iodine number of 39 and a molecular equivalent of 282, indicating a very impure sample of stearic acid.

Twenty-five per cent. of the ester used in the above procedure was not accounted for in the crystalline lithium salts. When the volume was readjusted for the weight of acid remaining in solution, the lithium salt still would not crystallize. The calcium salt of the acid was soluble in alcohol, and the barium salt could not be made to crystallize. After acetylation the saponification and neutralization numbers showed conclusively that an hydroxy acid was present. Purification of the remaining 3.2 g. by precipitation of the lead salt from alcohol and extraction with two 50-cc. portions of boiling petroleum ether, followed by acetylation, confirmed the presence of a $C_{18}$ monoethylenic hydroxy acid.

TABLE VII

THE HYDROXYOLEIC ACID OF RUVETTUS OIL

| | Saponification | | Neutralization | | Iodine | |
|---|---|---|---|---|---|---|
| | Number | Mol. wt. | Number | Mol. wt. | Number | Mol. wt. |
| Soluble Li salts after acetylation | 295.7 | 378 | 168 | 334 | 70.6 | 359 |
| Insol. Pb salt after acetylation | 349 | 321 | 169.6 | 330 | .. | ... |
| Calcd. for hydroxyoleic acid | 330 | 340 | 165 | 340 | 77.6 | 340 |

In connection with this acid it is to be noted that C. W. Moore[21] has isolated a dihydroxyoleic acid from the oil of a South Sea whale.

**Fraction 210–212°.**—The fatty acids of this fraction were treated by the procedures above; the acid from the lithium salt gave iodine numbers agreeing well with that for pure oleic acid. There was also present, though in smaller amount, soluble lithium salts. After acetylating the free acid from these the neutralization, saponification and iodine numbers were, respectively, 163.5, 298.2 and 74.2. These values are further confirmatory for the hydroxyoleic acid.

**Residue from Original Fractionation.**—The residue, 65 g., from the first fractionation of the esters, Table V, was refractionated at 5 mm.

TABLE VIII

REFRACTIONATION OF RESIDUE

| | to 200° | 200–205° | 205–215° | Residue |
|---|---|---|---|---|
| Weight, g. | 19.1 | 10.2 | 10.7 | 26.2 |
| Iodine no. | 86.5 | 90.0 | 90.9 | 81.3 |
| Sapon. no. | 211.5 | 216.0 | 206.6 | .. |

The low iodine values indicate that there is only a trace of unsaturation greater than mono-ethylenic. In confirmation of this, no ether-insoluble bromide could be isolated from the most highly unsaturated fraction.

[21] Moore, *J. Soc. Chem. Ind.*, **38**, 322T (1919).

The high saponification numbers were paralleled by high free acid and this was shown to be caprylic acid, due undoubtedly to decomposition. Because of this the two lower fractions were combined and redistilled at 9 mm., the main fraction boiling at 221–223° at this pressure. The saponification number (178) indicated gadoleic acid (calculated 181); iodine number, 76.4; calculated, 81.8. Complete identification of this acid was difficult; when hydrogenated with Adams' catalyst[22] the ester absorbed the theoretical amount of hydrogen, but the free acid melted at 65°—indicating a mixture; when oxidized according to the procedure of Lapworth and Mottram,[23] the dihydroxy acids obtained melted low, 118–121°, again indicating a mixture. Purification of the gadoleic acid from the contaminant oleic acid was accomplished by crystallizing a dilute alcoholic solution of their lithium salts. After freeing the acid from the first crystals it had a neutralization number of 181.8 (calculated 181), corresponding to a molecular weight of 305.4 (gadoleic acid, 310). The iodine number was 77.4 (gadoleic acid, 81.8).

**Fraction 205–215°.**—After saponification and distillation of the caprylic acid the free acids were treated by the lithium salt method. The acids from the first crop of crystals melted at 30° and had a molecular weight by titration of 343, and an iodine number of 64.2. Theoretical values for erucic acid, $C_{22}H_{42}O_2$, are 338 and 75. The acid obtained from the second crystals was liquid at room temperature but had a molecular weight of 338.1 and an iodine number of 71.5. This fraction is chiefly erucic acid.

**Residue.**—A small amount of lithium salts was isolated from the thick red oil left in the still. After repeated recrystallizations from various solvents, the neutralization number and iodine number of the free acid indicated a mixture of $C_{24}H_{46}O_2$ and $C_{26}H_{50}O_2$.

**Glycerol.**—The merest trace of glycerol could be detected, as the tribenzoate, in the aqueous residue from 200 g. of the oil, after saponification and separation of the saponifiable and unsaponifiable constituents.

**Unsaponifiable Fraction.**—No satisfactory method has been devised for the separation of higher saturated and unsaturated alcohols.[24] The best methods have seemed to be crystallization from acetone[25] and fractional distillation. Neither of these methods was satisfactory in our hands.

Edeleanu[26] reported the interesting fact that aromatic and cyclic unsaturated hydrocarbons are soluble in liquid sulfur dioxide, while paraffins and naphthenes are almost completely insoluble. Moore, Morrel and Egloff[27] and Zerner, Weiss and Opalski,[28] confirmed and extended this observation. When the total unsaponifiable fraction was treated with this solvent it was found that only the unsaturated constituents were dissolved, and that excellent separation could be obtained.

The extraction was performed in the usual type Soxhlet apparatus save that the condenser jacket was open at the top for the introduction of pow-

[22] R. Adams and R. L. Shriner, THIS JOURNAL, **45**, 2171 (1923).

[23] A. Lapworth and E. N. Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

[24] T. P. Hilditch and J. A. Lovern, *J. Soc. Chem. Ind.*, **48**, 359–365, 365–368 (1929).

[25] Y. Toyama, *Chem. Umschau*, **31**, 61–67, 153–155 (1924).

[26] L. Edeleanu, *Petroleum*, **9**, 862–864; *Bull. Am. Inst. Mining Eng.* 2313–2332 (1914).

[27] R. J. Moore, J. C. Morrel and G. Egloff, *Met. Chem. Eng.*, **18**, 396–402 (1918).

[28] Zerner, Weiss and Opalski, *Z. angew. Chem.*, **35**, 253–256 (1922).

dered carbon dioxide. When the extraction is complete, the condenser tube is attached to a rubber connection leading to a Dewar flask. The next morning the solvent is found in this flask and a new extraction begun.

A comparison of the separation afforded by the three methods is given in Table IX.

TABLE IX

SEPARATION OF SATURATED FROM UNSATURATED ALCOHOLS. COMPARISON OF METHODS

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Acetone | Melting points, °C. | | | 33–34 | | 36 | | 38 |
| | | I nos. of fractions distd. from last prod. | | | | | | | 12, 16 and 52 |
| 2 | Distillation | Fractions | 1 | 2 | 3 | 4 | 5 | 6 | 7 Residue |
| | | I nos. | 19 | 18 | 23 | 43 | 59 | 69 | 76 146 |

| | | | | Iodine numbers | | |
|---|---|---|---|---|---|---|
| | | Time of extn. | Extd., % | Original | Extract | Residue |
| 3 | $SO_2$ extraction | | | | | |
| | A | 5 hrs. | 47.0 | 58 | 106 | 13 |
| | B | 5 hrs. | 13.9 | 13 | 65 | 2.2 |

The efficiency of extraction is dependent on the fineness of the material, and it is advantageous, after the first extraction, again to shave the material. Some saturated alcohol is dissolved with the large amount of unsaturated material present, but fortunately the solubility of pure cetyl alcohol in liquid sulfur dioxide is very small.[29] The procedure may also be successfully applied to mixtures of fatty acids, but in this case a larger amount of saturated acid is dissolved.

**Fractionation of the Sulfur Dioxide Insoluble Fraction.**—One hundred and seven grams of the material insoluble in sulfur dioxide was acetylated and distilled at 15 mm.

TABLE X

DISTILLATION OF SATURATED ALCOHOL ACETATES

| | to 199° | 199–202° | 202–203° | Residue |
|---|---|---|---|---|
| Weights | 9.3 | 81.2 | 17.0 | 11.8 |
| Iodine nos. | 1.1 | 1.2 | 1.7 | 8.5 |
| Sapon. nos. | 196.1 | 194.2 | 186.3 | 182.9 |

**To 199°.**—This fraction, on redistillation, yielded 1.1 g. boiling below 190°; saponification number, 200.3. On crystallization of the alcohol from 90% ethyl alcohol, the crystals melted at 45–47°. The solid remaining after evaporation of the mother liquors melted at 38–40°—indicating the presence of a small amount of tetradecyl alcohol (m. p. 37.5°).

**Fraction 199–202°.**—The boiling point of this substance agrees well with the accepted value for cetyl acetate.[30] The saponification number of cetyl acetate is 197.5, the density (I. C. T.) $d_4^{20}$ 0.859; density found, $d_4^{25}$ 0.856. The alcohol obtained on saponification melted at 49.5°. This fraction is thus cetyl acetate.

**Fraction 202–203°.**—This was redistilled and the main portion identified as cetyl acetate. One gram, as a higher boiling fraction, had a saponification number of 189.5,

[29] W. F. Seyer and R. W. Ball, *Trans. Roy. Soc., Canada,* [3] **19,** 149–151 (1926).

[30] J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," The Macmillan Co., 6th ed., p. 244.

and the recrystallized alcohol melted at 57–58°, indicating the presence of octadecyl alcohol (m. p. 59°).

**Residue.**—The majority of this fraction, after saponification, was identified as octadecyl alcohol by its melting point, 58.5°.

**Fractionation of the Sulfur Dioxide Soluble Fraction.**—The fraction was distilled directly at 15 mm.

TABLE XI

DISTILLATION OF THE SULFUR DIOXIDE-SOLUBLE FRACTION

| | to 185° | 185–200° | 200–206° | Residue |
|---|---|---|---|---|
| Weights | 6.5 | 27.4 | 30.0 | 48.9 |
| Iodine nos. | 62.9 | 79.5 | 92.8 | 121.0 |

**Fraction 200–206°.**—The constants of this fraction agree with those given for oleyl alcohol: b. p. (15 mm.) 200–206°; I, no. 92.8; $n_D^{25}$ 1.4611; $d_4^{25}$ 0.860. Toyama[31] gives b. p. (15 mm.) 205–210°, $n_D^{20}$ 1.4607, $d_4^{20}$ 9.8489. Bouveault and Blanc[32] give b. p. (13 mm.) 200°, $d_4^0$ 9.862. The theoretical iodine number for oleyl alcohol is 94.7. This agreement makes the identity of the fraction certain.

**Fractions 185–200° and "to 185°."**—Cetyl alcohol boils at 189° at 15 mm., so that that dissolved by sulfur dioxide would appear in these fractions. This was the case, and no satisfactory method has been found to separate the cetyl and oleyl alcohols.

**Residue.**—The large residue is not surprising when it is remembered that no attempt was made to free the original unsaponifiable material from sterols and possible hydrocarbons. Part of the material was distilled at 1.5 mm., and the fraction 210–260° gave a small amount of squalene.

**Fraction 210–260° (1.5 mm.).**—One gram of this fraction was placed in 10 cc. of acetone and dry hydrogen chloride gas passed in until the solution was saturated. On cooling and concentrating, a small amount of white crystals separated which melted, after recrystallization, at 111–130°. Squalene[33] forms a hexahydrochloride which melts indefinitely between 112–126°.[34] This is confirmatory for the presence of this hydrocarbon.

The remaining residues resisted all attempts at further analysis.

**Cholesterol.**—The digitonin method of Windaus[35] for the separation of sterols was employed on a small sample of the total unsaponifiable fraction which had been previously washed with ice cold methyl alcohol. The flocculent precipitate obtained was washed with alcohol and ether, decomposed with boiling xylene, filtered and the residue from the evaporation of the xylene tested for the presence of cholesterol by the Burchard[36] and Salkowski[37] color reactions. Both were positive.

## Summary

1. The oil of *Ruvettus pretiosus* has been analyzed, and consists primarily of cetyl and oleyl esters of oleic and hydroxyoleic acids. The oil is best classified as a liquid wax.

[31] Y. Toyama, *Chem. Umschau*, **31**, 13–17 (1924).

[32] Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 1210 (1904).

[33] M. Tsujimoto, *J. Ind. Eng. Chem.*, **8**, 889 (1916); **12**, 63 (1920).

[34] I. M. Heilbron, E. D. Kamm and W. M. Owens, *J. Chem. Soc.*, 1630 (1926).

[35] A. Windaus, *Ber.*, **42**, 238–246 (1909).

[36] R. H. A. Plimmer, "Practical Organic and Biochemistry," Longmans, Green and Co., **1926**, p. 345.

[37] E. Salkowski and W. R. Orndorff, "Laboratory Manual of Physiological and Pathological Chemistry," John Wiley and Sons, Inc., New York, **1904**, pp. 91–92.

2. The constituents present are: acids—stearic, oleic, gadoleic, erucic, $C_{24}H_{46}O_2$, $C_{26}H_{50}O_2$, an hydroxyoleic acid; alcohols—oleyl, tetradecyl, cetyl, octadecyl, cholesterol, glycerol: hydrocarbon—squalene.

3. The purgative properties of the oil have probably been over-emphasized, although there does seem to be a modicum of pharmacological action. This may be dependent on its content of esters of higher alcohols.

4. Extraction with liquid sulfur dioxide has been shown to be a satisfactory method for the separation of the saturated and unsaturated constituents of the unsaponifiable fraction.

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

# ISOMERIC ALPHA-PARA-NITROPHENYL-BETA-PHENYL-DELTA-KETONIC ACIDS

BY S. AVERY, C. B. BISWELL AND E. E. LISTON

RECEIVED JULY 1, 1931 PUBLISHED JANUARY 7, 1932

Attempts to resolve the inactive isomeric α,β-diphenyl-δ-ketonic acids, described in a previous paper,[1] into optically active forms were unsuccessful. It was accordingly decided to synthesize the acids named in the title of this paper in the expectation that these would more readily permit the formation of optical isomers. Although attempts along this line up to the present had not been successful, these inactive nitro acids and their derivatives show certain properties markedly different from all delta-ketonic acids previously studied.

The two isomeric nitriles of α-p-nitrophenyl-β-phenyl-γ-benzoylbutyric acid have been investigated by Allen.[2] He appears, however, not to have interested himself in preparing the acids themselves and no further reference appears in the literature. Further, no work has been found bearing on α-p-nitrophenyl-β-phenyl-γ-trimethylacetylbutyric acid or its derivatives.

In condensing benzalpinacolone with methyl p-nitrophenylacetate in the presence of sodium methoxide, a crystalline substance was formed, easily purified, and without evidence of isomeric admixture. When, however, benzalpinacolone was condensed with ethyl p-nitrophenylacetate in the presence of sodium ethoxide, a crystalline substance was formed which hydrolyzed to an isomer of the one obtained by the methyl condensation route. Though the isomers melted with decomposition at the same temperature, the crystalline forms were distinctly different and their derivatives showed marked variations. An entirely similar result was obtained when benzalacetophenone was condensed, first with methyl p-

[1] Avery and Jorgensen, THIS JOURNAL, **52**, 3628 (1930).

[2] Allen, *ibid.*, **47**, 1733 (1925).

nitrophenylacetate in the presence of sodium methoxide, and later when ethyl *p*-nitrophenylacetate and sodium ethoxide were used. Isomeric, not identical, forms were obtained by the different routes. In the case of both series, those obtained by the methyl route crystallized, in general, as coarse needles or prisms; those by the ethyl route as fine needles or hairs. The derivatives of the acids obtained through the ethyl condensation, in general, melted higher than those obtained in a corresponding way through the methyl condensation. In order to distinguish between the two isomers, the authors will in this article designate the two series as the "E" series and the "M" series. Condensation of *n*-propyl and *n*-butyl esters in the presence of sodium dissolved in the corresponding alcohols, led to what we have termed the "E" series. Hydrolysis of the lower melting nitrile led to the "M" series; hydrolysis of the higher to the "E" series. The 126° ("M") nitrile described by Allen can, as he has pointed out, be transformed into the "E" or higher melting nitrile and, as the authors have found, the process can be in part reversed. The ethyl esters of the "M" series can be readily transformed into the corresponding esters of the "E" series by dissolving in ethyl alcohol and treating with sodium ethoxide. Both isomeric acids give distinct lactones which can be converted into their corresponding acids and esters.

In the benzoyl series, the amount of the nitriles formed is in the ratio of about 3 to 1 in favor of the "E" product while in the trimethylacetyl series the yield of the "E" nitrile is almost quantitative. While small amounts of the "E" derivative may be detected when the methyl route is followed in condensing the ester in the benzoyl series, it does not appear to be formed in the trimethylacetyl ester condensation.

Except for minor details the results obtained in both series show close analogy, and the distinction in the compounds formed in the methyl route from those formed in the ethyl route is equally characteristic in the case of the benzoyl and the trimethylacetyl derivatives.

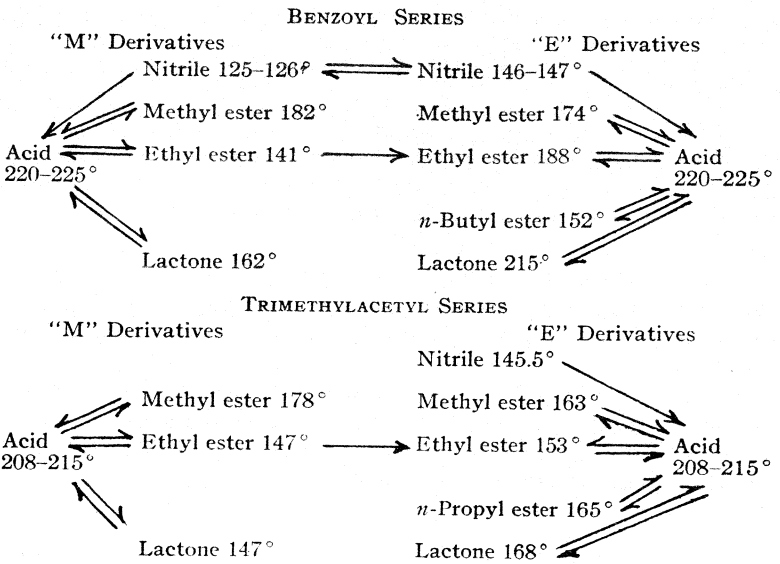
The diagram represents in a graphic way the relations of the several compounds mentioned.

## Experimental Part

### The Benzoyl Series

**The "M" Methyl α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyrate.**—Ten grams of methyl *p*-nitrophenylacetate and 10.1 g. of benzalacetophenone were dissolved in warm absolute methanol. After cooling, a solution of 1.2 g. of sodium dissolved in 20 cc. of methanol was added. The flask containing the mixture was immediately plunged into ice water and the contents stirred for a few minutes during which time a crystalline deposit separated. After standing for several hours, acetic acid was added to discharge the color. The pasty mass was taken up with ligroin, filtered and washed with water. Recrystallized from *n*-butyl alcohol or a mixture of methanol and chloroform, the compound separated in the form of beveled plates melting at 182°; yield, about 95%.

*Anal.* Calcd. for $C_{24}H_{21}O_5N$: C, 71.44; H, 5.25. Found: C, 71.42; H, 5.38.




**The "M" α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyric Acid.**—The ester just described was hydrolyzed by boiling in acetic acid solution with a mixture of equal parts of water and sulfuric acid added drop by drop over a considerable period of time. The product of hydrolysis was poured into water, filtered and washed, then dissolved in dilute ammonium hydroxide, filtered again and reprecipitated with hydrochloric acid. Recrystallized from acetic acid the acid separated in the form of pointed prisms melting with decomposition at 220–225°.

*Anal.* Calcd. for $C_{23}H_{19}O_5N$: C, 70.93; H, 4.92. Found: C, 70.57; H, 4.94.
*Titration.* 0.2116 g. required 5.17 cc. of *N*/10 NaOH. Calcd.: 5.15 cc.

**The "M" Ethyl α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyrate.**—This ester was formed by the action of ethanol and hydrogen chloride on the acid just described. Recrystallized from alcohol, it separated in the form of prisms melting at 141°.

*Anal.* Calcd. for $C_{25}H_{23}O_5N$: C, 71.91; H, 5.55; N, 3.36. Found: C, 72.01; H, 5.66; N, 3.46.

**The "M" α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyrolactone.**—A mixture of 2 g. of the "M" acid and 10 cc. of acetyl chloride was heated for fifteen hours in a sealed tube at a temperature of 60°. After evaporating off most of the acetyl chloride, the residue was taken up with a small amount of petroleum ether. On stirring, a crystalline mass formed which was further purified by recrystallizing from isobutyl alcohol, m. p. 162°.

*Anal.* Calcd. for $C_{23}H_{17}O_4N$: C, 74.37; H, 4.62. Found: C, 74.42; H, 4.68.

**The "M" α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyronitrile.**—It is very difficult to obtain this nitrile so wholly free from the "E" isomer that the product of saponification is not contaminated with the "E" acid, showing marked drop in the melting point. The acid obtained by hydrolyzing the "M" nitrile is readily converted into the ethyl ester from which the traces of the "E" ethyl ester can be separated through the comparative insolubility of this ester in alcohol.

**The "E" Ethyl α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyrate.**—Ethyl *p*-nitrophenylacetate was condensed with benzalacetophenone in ethanol solution with sodium ethoxide according to the directions given for the preparation of the "M" methyl α-*p*-

nitrophenyl-β-phenyl-γ-benzoylbutyrate. Twice recrystallized from a mixture of chloroform and ethanol, it melted at 188°.

*Anal.* Calcd. for $C_{25}H_{23}O_5N$: C, 71.91; H, 5.55; N, 3.36. Found: C, 71.72; H, 5.49; N, 3.36.

**The "E" α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyric Acid.**—This acid was obtained by the hydrolysis in acid solution of the "E" ethyl ester just described. Recrystallized from a mixture of ethyl acetate and glacial acetic acid, it separated in the form of long hair-like crystals melting with decomposition at 220–225°.

*Anal.* Calcd. for $C_{23}H_{19}O_5N$: C, 70.93; H, 4.92. Found: C, 71.03; H, 4.99.

*Titration.* 0.2651 g. required 6.75 cc. of *N*/10 NaOH. Calcd.: 6.83 cc.

**The "E" Methyl α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyrate.**—This ester was prepared from the "E" acid with methanol and hydrogen chloride. Recrystallized from methanol the compound melted at 174°.

*Anal.* Calcd. for $C_{24}H_{21}O_5N$: C, 71.44; H, 5.25. Found: C, 71.53; H, 5.29.

**The "E" *n*-Butyl α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyrate.**—This compound was obtained by the direct condensation of *n*-butyl *p*-nitrophenylacetate with benzalacetophenone in the presence of sodium dissolved in *n*-butyl alcohol. Recrystallized from *n*-butyl alcohol the compound separated in the form of slender prisms or needles melting at 152°.

*Anal.* Calcd. for $C_{27}H_{27}O_5N$: C, 72.77; H, 6.11. Found: C, 73.14; H, 6.14.

**The "E" α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyrolactone.**—A mixture of 1 g. of the "E" acid and 20 cc. of acetyl chloride was heated for five hours in a sealed tube at 110°. Petroleum ether was added, the product filtered, and recrystallized from tertiary amyl alcohol; yield, 85%, m. p. 215°.

*Anal.* Calcd. for $C_{23}H_{17}O_4N$: C, 74.37; H, 4.62. Found: C, 74.20; H, 4.63.

**The "E" α-*p*-Nitrophenyl-β-phenyl-γ-benzoylbutyronitrile.**—The hydrolysis of this nitrile in acid solution did not result in as pure a product as was obtained by the hydrolysis of the esters. However, the pure acid may be obtained by conversion of the impure acid into the 188° ethyl ester and hydrolysis of the same.

**Transformation: "M" Derivatives ⇌ "E" Derivatives.**—Allen has shown that the "E" nitrile may be obtained from the "M" nitrile by treating the latter with alkali.

The authors found that when 1 g. of the "E" (147°) nitrile was added to 50 cc. of approximately 99% ethanol, 10 mg. of sodium carbonate added, and the mixture refluxed for some time, solution was gradually accomplished with the change to a deep red color. After two hours, a drop of glacial acetic acid was added to discharge the color. On cooling and condensing to two-thirds its volume, 0.5 g. of the "E" nitrile separated. Further condensing with subsequent cooling led to an additional small amount of the "E" isomer, the filtrate yielding 0.2 g. of the "M" nitrile, m. p. 124–126°. It is evident that whether one starts with the lower or with the higher melting nitrile, a condition of equilibrium is soon reached in alkaline solution.

The "M" ethyl ester is transformed into the "E" ethyl ester by sodium ethoxide in ethanol solution. The transformation appears to be nearly quantitative.

## The Trimethylacetyl Series

The methods of preparation and purification of the members of this series of acids and derivatives were, in general, analogous to those described for the corresponding members of the benzoyl series. The "M" methyl ester, "E" ethyl ester, "E" *n*-propyl ester and the "E" nitrile were prepared by direct condensation of the corresponding ester or nitrile of *p*-nitrophenylacetic acid with benzalpinacolone. Hydrolysis of the "M"

methyl ester led to the formation of the "M" acid while hydrolysis of the "E" ethyl ester, "E" *n*-propyl ester, and the "E" nitrile resulted in the formation of the "E" α-*p*-nitrophenyl-β-phenyl-γ-trimethylacetylbutyric acid. The lactones were prepared in the usual manner.

The following table contains a brief summary of the data concerning the two isomeric α-*p*-nitrophenyl-β-phenyl-γ-trimethylacetylbutyric acids and their derivatives.

| Compound | Series | M. p., °C. | Analysis, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|
| Acid | "M" | 208–215 | 68.26 | 6.28 | 68.13 | 6.30 |
| Methyl ester | "M" | 178 | 68.89 | 6.58 | 68.84 | 6.63 |
| Ethyl ester | "M" | 147 | 69.48 | 6.85 | 69.30 | 6.85 |
| Lactone | "M" | 147 | 71.76 | 6.03 | 71.86 | 6.06 |
| Acid | "E" | 208–215 | 68.26 | 6.28 | 68.23 | 6.30 |
| Nitrile | "E" | 145.5 | 71.97 | 6.30 | 71.76 | 6.29 |
| Methyl ester | "E" | 163 | 68.89 | 6.58 | 68.90 | 6.61 |
| Ethyl ester | "E" | 153 | 69.48 | 6.85 | 69.50 | 7.03 |
| *n*-Propyl ester | "E" | 165 | 70.03 | 7.11 | 69.90 | 7.13 |
| Lactone | "E" | 168 | 71.76 | 6.03 | 71.62 | 5.96 |

The "M" ethyl ester of this series, like the corresponding ester in the benzoyl series, can be transformed into the "E" ethyl ester by dissolving in ethyl alcohol and treating with sodium ethoxide.

Efforts to transform derivatives of the "E" series into those of the "M" series were unsuccessful.

**Comparison of the Trimethylacetyl Derivatives with the Benzoyl Derivatives.**—In the case of the trimethylacetyl derivatives, no mixtures of isomers were evident in any of the condensations. All condensations led to members of the "E" series except the condensation of methyl *p*-nitrophenylacetate with benzalpinacolone in the presence of methanol and sodium methoxide. The trimethylacetyl derivatives crystallized more readily than the benzoyl derivatives and were more easily prepared in pure condition. Aside from these facts, the two series closely parallel each other.

The authors are indebted to Mr. J. M. Brackenbury, Mr. Kenneth Majors and Mr. Frank McGrew for assistance in preparing these compounds and in doing analytical work, and to Dr. W. D. Maclay for assisting in preparing the communication for publication.

## Summary

Isomeric α-*p*-nitrophenyl-β-phenyl-γ-benzoylbutyric acids and a number of their derivatives have been prepared.

Isomeric α-*p*-nitrophenyl-β-phenyl-γ-trimethylacetylbutyric acids and their derivatives have also been prepared and compared with the preceding.

In preparing the nitriles of these acids through direct condensation, methanol and ethanol may be used interchangeably, or mixed, as a solvent without influencing the result.

In the condensation with methyl esters, sodium methoxide in the presence of methanol leads to one of the isomeric series ("M"); while in the case of the ethyl esters, sodium ethoxide in the presence of ethanol leads to the other series ("E"). *n*-Propyl esters in *n*-propyl alcohol, and *n*-butyl

esters in *n*-butyl alcohol lead to the same series ("E") as is obtained by the ethyl condensation. The "E" series is the more stable form. Through the selection of esters, condensing agents and solvents, either series may be made at pleasure.

LINCOLN, NEBRASKA

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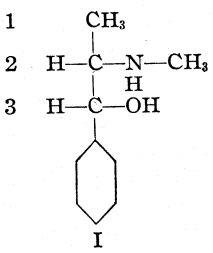
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# STUDY ON THE CONFIGURATION OF EPHEDRINE[1]

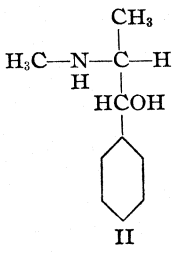
BY KARL FREUDENBERG,[2] EUGENE SCHOEFFEL AND EMIL BRAUN

RECEIVED JULY 16, 1931 PUBLISHED JANUARY 7, 1932

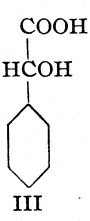
The configurational relationship of ephedrine and pseudoephedrine (I or II)[3] has been discussed by different investigators[4] from the viewpoint that in one of the two stereoisomers the OH group is located nearer to the $NHCH_3$ group than in the other.



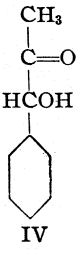
I



II



III



IV

Since the bond between carbon atoms 2 and 3 is free to rotate, the two groups can approach each other in the same way in both substances. We do not believe that any evidence with regard to the configuration can be given in this way.

The only possible way of solving the problem would be to bring the two asymmetric carbon atoms in steric correlation with substances of known configuration.

This has been carried out for carbon atom 3 in the following manner. The amide of *d*-mandelic acid (III) forms with methylmagnesium iodide the levorotatory phenylacetylcarbinol IV. This reaction was carried out with the inactive material by H. Wren,[5] whose method has been improved. The rotation of our carbinol IV is lower (about two-thirds)

[1] Steric series No. 15; preceding communication, *Ber.*, **64**, 703 (1931).

[2] Carl Schurz Memorial Professor for 1931 at the University of Wisconsin.

[3] A report on the ephedrine alkaloids is given by K. K. Chen and C. H. Kao, *J. Am. Pharm. Assocn.*, **15**, 625 (1926); *cf.* K. K. Chen and C. F. Schmidt, *Medicine*, **9**, 1 (1930).

[4] E. Schmidt, *Arch.*, **252**, 89 (1914); E. Späth and R. Göhring, *Monatsh.*, **41**, 319 (1920); H. Emde, *Helv. Chim. Acta*, **12**, 365 (1929).

[5] Wren, *J. Chem. Soc.*, **95**, 1592 (1909).

than a levorotatory carbinol obtained by C. Neuberg[6] when sugar was fermented in presence of benzaldehyde.

By means of our synthesis the configuration of the carbinol is established although we do not claim that our substance is homogeneous. The carbinol was dissolved in an alcoholic solution of methylamine and immediately hydrogenated. From the reaction product *l*-ephedrine was isolated as the only basic substance formed. Natural *l*-ephedrine has therefore the configuration I or II. Since it can be transformed by conversion of the carbinol group into natural *d*-pseudoephedrine, this base has the opposite configuration of the carbinol group.

In preliminary experiments the synthesis was carried out with racemic mandelic acid, *d,l*-ephedrine being obtained. Experiments are in progress to establish the configuration of carbon atom 2.

## Experimental Part

Fifty grams of *dl*-mandelamide or *d*-mandelamide[7] prepared from amygdalin was slowly added to a well-cooled Grignard solution of 240 g. of methyl iodide, 48 g. of magnesium and 700 g. of ether. The mixture was gently boiled for sixteen hours, decomposed with dilute sulfuric acid and extracted with ether; 40 g. of a light yellow oil was obtained which was distilled under a pressure of 15–18 mm. The fractions boiling between 110–125° (7 g.) and 125–140° (28 g.) contained the active carbinol; $[\alpha]_D$ of the active carbinol in 2% absolute alcohol solution, −108°. The same fractions gave a semicarbazone melting at 192° (from the *dl*-amide) and at 189° (from the active amide). These melting points are in agreement with observations made by C. Neuberg[6] and K. v. Auwers.[8]

Six grams of levorotatory phenylacetylcarbinol, 2 g. of palladium black and 30 cc. of a 25% alcoholic solution of methylamine were hydrogenated at pressures of 1 and of 20 atmospheres.[9] In the first case 450 cc. of hydrogen was absorbed, which is 30% of the theoretical. The yield of ephedrine is rather independent of the pressure.

After evaporation of the alcohol and methylamine under reduced pressure a sirupy mass was obtained which was taken up in 2 cc. of warm alcohol and 10 cc. of a dry ethereal solution of hydrochloric acid added. A dark brown oil separated which began to crystallize after washing twice with 10 cc. of absolute ether. The crystalline mass was then washed with 2 cc. of dry chloroform, the white crystals filtered, dissolved in 2 cc. of absolute alcohol and recrystallized by careful addition of absolute ether. The chloroform filtrate was made alkaline, extracted with ether for seventy-two hours, the ether extract acidified with dry hydrochloric acid, and the brown oil separating out was treated as above, yielding a second somewhat impure crystallization product which may contain a stereoisomer. The crystals of the first portion (0.8 g.) melted at 218° with decomposition; $[\alpha]_D^{20}$ in absolute alcohol, $-0.32° \times 6/1 \times 0.060$ g. = −32° (± 2).

*Anal.* Subs., 5.1 mg.: 0.330 cc. N (740 mm., 20°). Calcd.: N, 6.97. Found: N, 7.11.

A sample of natural *d*-ephedrine hydrochloride decomposed at 215–216° (a mix-

[6] Neuberg, *Biochem. Z.*, **128**, 613 (1922).

[7] K. Freudenberg and L. Markert, *Ber.*, **58**, 1753 (1925).

[8] Auwers, *Biochem. Z.*, **192**, 227 (1928).

[9] Feulgen, *Ber.*, **54**, 360 (1921); F. Knoop, *Z. physiol.*, **148**, 290 (1925).

ture at 213°) and had an $[\alpha]_D^{20}$ −33° (E. Späth and R. Göhring[10] indicate −34.5° in water and a decomposition point of 217–218°).

From *dl*-mandelic amide, *dl*-ephedrine was obtained. The hydrochloride melted with decomposition at 183° (E. Späth and R. Göhring[10] indicate a decomposition point of 188–189.5).

*Anal.* Subs., 5.050 mg.: 0.295 cc. N (740 mm. 20°). Calcd.: N, 6.97. Found: N, 6.72.

The salt was dissolved in absolute alcohol and dry barium hydroxide added. When the barium-free filtrate was mixed with petroleum ether, the free base began to crystallize out; m. p. 74.5°. Späth and Göhring indicate 73–74°.

*Anal.* Subs., 2.4 mg.: 0.183 cc. N (740 mm. 20°). Calcd.: N, 8.48. Found: N, 8.38.

## Summary

*l*-Ephedrine has been synthesized from *d*-mandelic acid and the the configuration at the carbinol group shown.

MADISON, WISCONSIN, AND HEIDELBERG, GERMANY

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[A CONTRIBUTION FROM THE CHEMICAL LABORATORIES, UNIVERSITY OF MISSOURI]

# SOME REACTIONS OF DI-HALOGEN BARBITURIC ACIDS

BY DOROTHY NIGHTINGALE AND ARTHUR EDWARD SCHAEFER

RECEIVED JULY 16, 1931 PUBLISHED JANUARY 7, 1932

The 5,5-di-halogen barbituric acids have been known since 1864, but there is relatively little in the literature concerning their reactions. Baeyer[1] observed that there was a difference in the reactivity of the two halogens in 5,5-dibromobarbituric acid and states that one bromine is more readily replaced than the other. Trzcinski[2] reports the reaction of dibromobarbituric acid with thiourea and with potassium or ammonium thiocyanate. Whiteley[3] prepared the hydrazone of 1,3-diphenylalloxan from 5,5-dibromo-1,3-diphenylbarbituric acid and phenylhydrazine. Biltz and Hamburger[4] developed a method for the preparation of monobromobarbituric acid from the dibromobarbituric acid and ammonia.

These facts suggested the possibilities of reactions of various classes of nitrogen compounds, such as amines, carbazides, acid amides, etc., not only with the dibromobarbituric acid but also with the corresponding dichloro derivative.

Since one molecule of thiourea or one molecule of phenylhydrazine reacts with the dibromobarbituric acid with the elimination of two molecules of hydrogen bromide, it was expected that primary amines would

[10] Späth and Göhring, *Monatsh.*, **41**, 319 (1920).

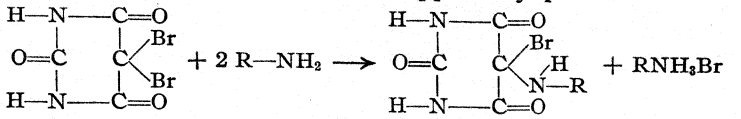
[1] Baeyer, *Ann.*, **130**, 33 (1864).

[2] Trzcinski, *Ber.*, **16**, 1057 (1883).

[3] Whiteley, *J. Chem. Soc.*, **91**, 1334 (1907).

[4] Biltz and Hamburger, *Ber.*, **49**, 635 (1916).

react similarly. However, only one bromine was found to react with either primary or secondary amines to form a 5-bromo-7-R- or a 5-bromo-7-$R_2$-uramil, respectively. The reaction apparently proceeds as follows




Alcohol was used as the solvent for the reaction. If the amine is added directly to the dibromobarbituric acid, a vigorous reaction occurs with charring and some tar formation.

Dibromobarbituric acid reacted normally with α-naphthylhydrazine, forming the α-naphthylhydrazone of alloxan. The 4,4-diphenyl semicarbazide and dibromobarbituric acid react readily to form a diphenyl semicarbazone of alloxan.

Other compounds which reacted with dibromobarbituric acid were formamide, formanilide and benzyl formate, but the results could not be interpreted satisfactorily.

As might be expected, dichlorobarbituric acid was relatively unreactive. In alcohol solution it did not react with any of the amines except benzyl and dibenzyl amines, but if the primary amine was added directly to the dichloro acid, a moderate reaction occurred with the formation of a dark gummy mass which would not yield crystals. It reacted with α-naphthylhydrazine and with 4,4-diphenyl semicarbazide.

## Experimental

The condensation products of primary and secondary amines with dibromobarbituric acid are easily prepared. For the most part they are nearly colorless crystalline compounds, though some of them have a tendency to turn pink on standing. They are soluble in water, somewhat soluble in hot alcohol and insoluble in other usual organic solvents. Alkali decomposes them with the liberation of the amine. All of the condensation products were analyzed quantitatively for nitrogen and a quantitative bromine analysis was made on typical members of each series.

The reactions of ethylamine and of diethylamine with dibromobarbituric acid are typical of the reactions of the amines with the dihalogen barbituric acids.

**5-Bromo-7-ethyl-uramil.**—Seven grams (1 mol) of dibromobarbituric acid are dissolved in the smallest amount of hot alcohol. To this is added 3.6 g. (2 moles) of ethylamine. The ethylamine used was a 33% solution in water. The mixture was warmed and stirred vigorously. After a few minutes a pink crystalline solid separated from the solution. The crystals were collected on a Büchner funnel and washed with hot alcohol to remove any amine salt or dibromobarbituric acid. After repeated washing with warm alcohol, the melting point of the crystals was found to be 185° with decomposition. The compound shrinks at 180°; yield 3.5 g. or 57%; soluble in cold water and hot alcohol, insoluble in ether, benzene, acetone and chloroform.

**5-Bromo-7-diethyl-uramil.**—Four grams (2 mols) of diethylamine was added with stirring to an alcoholic solution of seven grams (1 mol) of dibromobarbituric acid. After warming the reaction mixture for a few minutes, almost colorless fine needles separated rapidly. They were collected on a Büchner funnel and washed with warm alcohol to remove any contaminating amine salt or unchanged dihalogen barbituric acid. The purified product melted with decomposition at 167–168°; yield, 5 g., or 74%; soluble in cold water and hot alcohol, insoluble in ether, benzene, chloroform and acetone.

These procedures were used with all of the other primary and secondary amines listed in Table I.

TABLE I

SUMMARY OF THE REACTION PRODUCTS OF PRIMARY AMINES AND DIBROMO BARBITURIC ACID

| Amine | M. p. of product, °C.[a] | Nitrogen analyses, % Calcd. | Found |
|---|---|---|---|
| Ethyl | 185 | 16.80 | 16.96 |
| Methyl | 175–176 | 17.79 | 17.85 |
| Butyl | 178 | 15.10 | 14.84 |
| Allyl | 179–180 | 16.03 | 16.20 |
| Benzyl | 186 | 13.46 | 13.75 |
| Ethanol | 159 | 15.78 | 16.03 |
| Diethyl | 167–168 | 15.10 | 15.11 |
| *n*-Dipropyl | 216 | 13.72 | 13.95 |
| *n*-Diamyl | Chars at 273 | 11.59 | 11.72 |
| Diisoamyl | 304 | 11.59 | 11.69 |
| Dibenzyl | 242 | 10.65 | 10.44 |

[a] All melting points are with decomposition.

TABLE II

HALOGEN ANALYSES (THOMPSON AND OAKDALE)

| Amine | Bromine analyses, % Calcd. | Found |
|---|---|---|
| Ethyl | 32.00 | 31.97 |
| Ethanol | 30.07 | 30.17 |
| Diethyl | 28.77 | 28.90 |
| Benzyl | 25.63 | 25.10 |
| Dibenzyl | 19.90 | 19.81 |

**Benzylamine and Dibenzylamine with Dichlorobarbituric Acid.**—These amines react readily with dichlorobarbituric acid, but the solubilities of the condensation products and the amine hydrochlorides are so similar that it was not possible to separate the hydrochlorides completely from the condensation products.

Butylaniline, isoamylaniline and diphenylamine did not react with either of the di-halogen barbituric acids even after long boiling of the alcohol solution.

Aromatic amines such as aniline, methylaniline, dimethylaniline, the toluidines, etc., when added to the halogen barbituric acids gave a dark tarry oil which would not yield crystals.

**Alloxan α-Naphthylhydrazone.**—A glacial acetic acid solution of 3.4 g. of α-naphthylhydrazine was added to 5 g. of dibromobarbituric acid dissolved in the smallest amount of hot glacial acetic acid. The mixture was boiled gently for a few minutes, then cooled to room temperature and poured into water. The brick red crystals which separated were collected on a Büchner funnel and washed with hot alcohol; melting

point, 264°, yield, 4 g. or 85%. The compound contains no bromine, is slightly soluble in hot alcohol, acetone and chloroform, and is insoluble in benzene, water and ether.

*Anal.* (Modified Kjeldahl). Calcd. for $C_{14}H_{10}N_3O_4$: N, 19.85. Found: N, 19.06.

The product formed in the same way from dichlorobarbituric acid and α-naphthylhydrazine was identical, melting at 264°. A melting point of mixtures of the two products was also 264°.

**Dibromobarbituric Acid and 4,4-Diphenyl Semicarbazide.**—A hot alcohol solution of 4 g. of dibromobarbituric acid was added to 3.2 g. of 4,4-diphenyl semicarbazide dissolved in alcohol. After warming the solution for a few minutes, 4 g. of a fine yellow powder separated, which after recrystallizing melted at 267°, with decomposition. It contained no bromine.

*Anal.* (Dumas) Calcd. for $C_{17}H_{13}N_5O_4$: N, 19.93. Found: N, 19.95.

This semicarbazone of alloxan is soluble in hot alcohol and insoluble in the other usual organic solvents.

Dichlorobarbituric acid reacted slowly with 4,4-diphenyl semicarbazide under the same conditions, but was expected to give the same semicarbazone of alloxan. However, the orange-yellow product, insoluble in alcohol and containing chlorine, was apparently a mixture which could not be purified. It contained 20.17% of nitrogen (Dumas) and 8.25% chlorine.

## Summary

1. Further evidence is presented showing that one halogen in the 5,5-dihalogen barbituric acids is more reactive than the other.

2. Dibromobarbituric acid reacts readily with primary and secondary amines with the loss of one molecule of hydrogen bromide.

3. Dichlorobarbituric acid is much less reactive than the dibromo compound, reacting readily only with benzylamines.

COLUMBIA, MISSOURI

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[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF THE PETROGRAD ACADEMY OF SCIENCE]

# FORMATION OF NAPHTHENIC ACIDS[1]

BY A. D. PETROV AND I. Z. IVANOV

RECEIVED JULY 24, 1931 PUBLISHED JANUARY 7, 1932

The mechanism of the formation of naphthenic acids present in petroleum is explained by two theories. According to C. Engler[2] naphthenic acids could have been formed[2] by cracking and cyclization of unsaturated fatty acids, which are considered as one of the original substances from which petroleum was formed, or[3] by oxidation of naphthenes and polynaphthenes with air. G. Kraemer and Weger[3] are in favor of the first theory from their experiments with acids from montan wax, while Kharichkov[4] prefers the

[1] Translated from the manuscript, by K. T. Steik.

[2] Engler, "Das Erdoel," Vol. I, **1911**, p. 452.

[3] Kraemer and Weger, *Chem.-Ztg.*, **31**, 675–77, 734 (1907); *Chem. Zentr.*, II, 734 (1907).

[4] Kharichkov, *J. Russ. Phys.-Chem. Soc.*, **40**, 1757 (1908); *Chem. Abstracts*, **3**, 1761 (1909).

oxidation theory on the basis of his laboratory experiments in which he oxidized petroleum with air. In neither case were indisputable proofs produced for the formation of naphthenic acids analogous to natural acids. This was due mainly to shortage of material. According to Kobayashi[5] naphthenic acids are formed when fish fats are distilled at atmospheric pressure. We[6] observed that naphthenic acids are formed when linoleic acid is cracked under pressure.

We had at our disposal a considerable amount of synthetic acids from two sources, namely, from cracking of oleic acid under pressure and from oxidation of gas oil distillate from Emba crude oil with air on a semi-manufacturing scale. Thus, it was possible for us to make closer investigation for determining whether the acids from cracking and those from oxidation belong to the group of saturated fatty acids or the group of naphthenic acids. We used a method similar to that of N. D. Zelinskii[7] for natural naphthenic acids, namely, we converted the acids into esters, alcohols, iodides and finally into the corresponding hydrocarbons. The amount of acids available was not sufficient for determining their structures and we worked therefore with wider fractions than those used by Zelinskii.

Analyses of hydrocarbons showed that in the first instance (cracking of oleic acid) at least part of them belongs to the naphthene series, while the hydrocarbons from acids from the other source are completely naphthenes. When considering the fact that products analogous with each other and with those from natural acids were obtained from two different starting materials and by different processes, it is reasonable to assume that in nature naphthenic acids were formed in both ways. Such a conclusion explains an observation made by L. Gurwitsch[8] that petroleum from deep layers of Bibi-Eibat and Balakhanui contains more naphthenic acids than petroleum from Surakhanui, which is located much nearer to the surface. Such a case would be impossible if naphthenic acids were formed by air-oxidation of naphthenes only.

## Experimental Part

Oleic acid was cracked in a two-liter autoclave in the presence of water and alumina at 380–390° and during three to four hours; 300 cc. of acid, 100 cc. of water and 10 g. of alumina were taken for each experiment. The highest pressure reached was 210–220 atmospheres, which dropped to 25–30 atmospheres on cooling. About four kilograms of oleic acid was treated in that way.

The cracked products were distilled into two fractions, the gasoline fraction up to 200° and the kerosene fraction from 200–280°. Ten per cent. of acids were isolated

[5] Kobayashi, *J. Chem. Ind. Japan*, **24**, 1–26 (1921); *Chem. Abstracts*, **15**, 2542 (1921).

[6] Petrov, *Ber.*, **63B**, 75–84 (1930); *J. Russ. Phys.-Chem. Soc.*, **61**, 1849–1859 (1929); *Chem. Abstracts*, **24**, 2696 (1930).

[7] Zelinskii, *Ber.*, **57B**, 42–51 (1924); *Chem. Abstracts*, **18**, 2148 (1924).

[8] Gurwitsch, "Scientific Foundation of Petroleum Technology," London, **1926.**

from the kerosene fraction by the Spitzer–Hoenig[9] method. After two fractionations 130 g. of acids was obtained. They distilled over between 211–250° and had a specific gravity of 0.9220 and an iodine number of 11.0.

Thus unsaturated acids were present only in small quantities.

Methyl esters were prepared from the mixture of these acids. They had a pleasant fruity odor. The crude esters distilled over at 150–220°. They were fractionated and the fraction boiling between 180–220° was used in further operations. The redistilled esters had a refractive index of 1.4239 (at 15°) and their ultimate analysis showed 69.05% carbon and 11.33% hydrogen.

The esters were converted into alcohols by the Bouveault method.[10] They distilled between 170–220°, had a refractive index of 1.4419 (at 15°) and contained 76.75% carbon and 13.22% hydrogen.

The alcohols were converted into iodides by means of iodine and phosphorus and these in turn were converted into the corresponding hydrocarbons by reduction with zinc dust in an alcoholic medium. Due to losses during these operations, only about two grams of hydrocarbons was obtained.

The hydrocarbons were treated with sulfuric acid to remove the unsaturates and they were subsequently distilled over metallic sodium. They distilled between 100–170°, had a specific gravity of 0.780, refractive index of 1.417. Their ultimate analysis was: C, 85.89; H, 14.62; calculated for $C_nH_{2n}$: C, 85.60; H, 14.40.

The analytical data correspond quite closely to values for octonaphthene carboxylic acid, nonanaphthene alcohol and nonanaphthene, which would approximately represent the average of the investigated wide fractions of esters, alcohols and hydrocarbons.

The presence of acids of the methane series in the cracked acids is indicated by the somewhat low specific gravity of these acids and by the high hydrogen content of the ester and alcohol fractions.

**Naphthenic Acids Obtained by Oxidation of Emba Gas Oil.**—The products of oxidation of Emba gas oil were obtained on a semi-manufacturing scale by G. S. Petrov. The gas oil, previous to oxidation, was treated with fuming sulfuric acid. The distillate was oxidized for the purpose of obtaining acids suitable for soap making. The oxidation was effected by air-blowing at 90–100° in the presence of catalysts. Oxy acids and carboxylic acids were obtained. The oxy acids decomposed into hydrocarbons during distillation at atmospheric pressure, while the carboxylic acids, which distilled without decomposition, were soluble in benzene and had a specific gravity below one.

The carboxylic acids were separated from the oxy acids by dissolving them in benzene and by repeated fractionation. The fraction distilling between 290–360° (at atmospheric pressure) was used in further investigations.

Acids of this fraction were purified according to the Spitzer and Hoenig[9] method and were then converted into their esters. For this purpose a mixture of 200 g. of acids, 400 g. of methyl alcohol and 50 g. of sulfuric acid (1.84 specific gravity) was heated on a water-bath for twenty hours. The excess of alcohol was then distilled off and the esters were washed with alkali and water. These esters had a pleasant fruity odor and distilled between 100–230° (at 1–3 mm. pressure). A portion of the 100 g. of esters obtained was saponified and converted into acids. These acids had a neutralization value of 135 and an iodine number of 0.7, while the saponification number of esters was 185.

The esters were converted into alcohols by the Bouveault–Blanc method. The following proportions of reagents were used: esters 80 g., absolute alcohol 240 g. and metallic sodium 25 g. The alcohols distilled between 100–212° (at 3–5 mm. pressure).

[9] Spitzer and Hoenig, *Monatsh.*, **39**, 1–14 (1918); *Chem. Abstracts*, **13**, 131 (1919).

[10] Bouveault, *Compt. rend.*, **136**, 1676 (1903); *Brit. Chem. Abstracts*, **84**, [I] 597 (1903).

They were a mobile straw-colored liquid with an odor similar to that of coriander oil. A portion of the alcohols was converted into acetates. The following proportions were used for this conversion: alcohols 10 g., fused sodium acetate 10 g. and acetic anhydride 40 g. Eight grams of acetates, with an acetyl number of 131, was obtained.

In the next step alcohols were converted into iodides. From 10 g. of alcohols, 1 g. of red phosphorus and 10 g. of iodine, 10 g. of iodides was obtained. The iodides were reduced to hydrocarbons by the Zelinskii method with zinc dust in an aqueous alcoholic medium; 5 g. of hydrocarbons was obtained. The distillation range of these hydrocarbons at 45 mm. pressure was 160–260°. The hydrocarbons did not dissolve in sulfuric acid and did not discolor bromine.

*Anal.* Calcd. for $C_nH_{2n}$: H, 14.38; C, 85.62. Found: H, 14.04; C, 85.84.

The hydrocarbons were dehydrogenated with sulfur and brominated with aluminum bromide according to Gustavson's method. Hydrogen sulfide evolved during the dehydrogenation and an oil was obtained as the reaction product. The bromination was accompanied by evolution of hydrogen bromide and resulted in a salve-like product. The hydrocarbon radical of these carboxylic acids is therefore of the naphthene type, mostly of the monocyclic type judging by the analytical data.

## Summary

Oleic acid was cracked in presence of water and alumina. Esters, alcohols and iodides were prepared and the latter finally converted to hydrocarbons. These corresponded to structures of octonaphthene and nonanaphthene type.

Emba gas oil was oxidized by air blowing at 90 to 100° in presence of catalysts, giving oxy and carboxy acids of monocyclic naphthene type.

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[CONTRIBUTION FROM THE LABORATORY FOR PURE RESEARCH OF MERCK AND CO., INC.]

# PREPARATION AND PROPERTIES OF ALPHA- AND BETA-METHYLCHOLINE AND GAMMA-HOMOCHOLINE[1]

BY RANDOLPH T. MAJOR AND JOSEPH K. CLINE

RECEIVED JULY 24, 1931 PUBLISHED JANUARY 7, 1932

A good deal of work has been devoted to the study of choline, its homologs and derivatives because of their interesting physiological properties.[2] Among the more important of the homologs of choline that have been investigated are those in which the hydroxyethyl group of choline has been replaced by the hydroxypropyl or hydroxyisopropyl group. Thus, α-methylcholine, $(CH_3)_3N(OH)CH(CH_3)CH_2OH$, β-methylcholine, $(CH_3)_3N(OH)CH_2CH(OH)CH_3$, and γ-homocholine, $(CH_3)_3N(OH)CH_2CH_2CH_2OH$, have been synthesized. A search through the literature has shown that there is considerable disagreement as to the properties of each of these compounds. Also, various investigators have

[1] Presented at the Indianapolis Meeting of the American Chemical Society April, 1931.

[2] Fraenkel, "Arzneimittel-Synthese," Julius Springer, Berlin, 1927, p. 336.

not agreed as to which isomer they have obtained when they have used the same method of preparation.

Morley[3] prepared what he termed "trimethyloxyisopropylammonium chloride" with the formula $(CH_3)_3N(Cl)CH(CH_3)—CH_2OH$ by the action of a solution of trimethylamine in alcohol on propylene chlorohydrin. Later Morley and Green[4] pointed out that Morley's propylene chlorohydrin was largely $CH_3CHOH—CH_2Cl$, which suggested that the compound to which Morley gave the structure $(CH_3)_3N(Cl)CH(CH_3)CH_2OH$ was at least to a large extent $(CH_3)_3N(Cl)CH_2CH(CH_3)OH$.

In 1911 Menge[5] prepared a compound which he called "α-methylcholine" by the action of a solution of trimethylamine in alcohol on a propylene chlorohydrin, prepared by the method of Henry,[6] which was supposed to have the formula $CH_3CHClCH_2OH$. Later Smith[7] showed that the propylene chlorohydrin, prepared by Henry's method, as well as the chlorohydrin used by Morley, consisted largely of $CH_3CHOHCH_2Cl$ with some of its isomer $CH_3CHClCH_2OH$. This suggests that Menge's "α-methylcholine" was probably the same as the compound or compounds obtained by Morley.

In 1922 Karrer[8] described the preparation of an "α-methylcholine" which had entirely different properties from Menge's "α-methylcholine." He obtained the iodide of his compound by the action of methyl iodide on the reduction product of the ethyl ester of N-dimethylalanine, $CH_3CH(N(CH_3)_2)COOC_2H_5$.

We have repeated the synthesis of the α-methylcholine chloride described by Karrer[9] and have obtained the same results that he did. However, we did find that his intermediate, the ethyl ester of N-dimethylalanine, could be somewhat more easily synthesized by the condensation of dimethylamine with ethyl α-bromopropionate than by his process.

The preparation of a so-called "β-methylcholine," first described in 1910 by Malengreau and Lebailly,[10] was effected by the action of a solution of trimethylamine in alcohol on propylene chlorohydrin, b. p. 128°. The properties of this "β-methylcholine" were very much like those of Menge's "α-methylcholine." Malengreau himself later pointed this out in a personal communication to the editors of Beilstein's "Handbuch der organischen Chemie,"[11] and suggested that since his "β-methylcholine" was the

[3] Morley, *Ber.*, **13**, 1805 (1880); *Compt. rend.*, **91**, 333 (1880).

[4] Morley and Green, *Ber.*, **18**, 24 (1885).

[5] Menge, *J. Biol. Chem.*, **10**, 400 (1911).

[6] Henry, *Bull. sci. acad. roy. Belg.*, 410 (1903); 734 (1906).

[7] Smith, *Z. physik. Chem.*, **93**, 83 (1918).

[8] Karrer, *Helv. Chim. Acta*, **5**, 477 (1922).

[9] Ref. 8, 476.

[10] Malengreau and Lebailly, *Z. physiol. Chem.*, **67**, 40 (1910).

[11] F. Beilstein, "Handbuch der organischen Chemie," Julius Springer, **1929**, 4th ed., Vol. 4, First Supplement, p. 433.

same as Morley's and Menge's "$\alpha$-methylcholine," the propylene chlorohydrin with the formula $CH_3CH(OH)-CH_2Cl$ must suffer rearrangement when it interacts with trimethylamine and gives $(CH_3)_3N(Cl)CH(CH_3)-CH_2OH$ instead of $(CH_3)_3N(Cl)CH_2CH(CH_3)OH$ as would be expected.

Berlin[12] in 1911 obtained a compound which he called "$\beta$-methylcholine" that had different properties from those ascribed to it by Malengreau and Lebailly. The salts of this "$\beta$-methylcholine" had the same properties as those ascribed by Partheil[13] to one of his "$\gamma$-homocholines" which will be discussed later. Berlin suggested that Partheil's "$\gamma$-homocholine" must also be "$\beta$-methylcholine."

We have found that catalytic reduction of trimethylacetonylammonium chloride, prepared by a slight modification of the method of Niemilowicz,[14] gave a compound which presumably must be $\beta$-methylcholine chloride, $(CH_3)_3N(Cl)CH_2CHOHCH_3$. The properties of this compound as well as those of its salts and esters corresponded in every way with those of a compound obtained by the condensation of a solution of trimethylamine in benzene with a propylene chlorohydrin which boiled at 125–128°. The properties of the salts and esters of this $\beta$-methylcholine compared very closely to those of the corresponding derivatives of Menge's[15] "$\alpha$-methylcholine" and of Malengreau and Lebailly's[10] "$\beta$-methylcholine."

Weisz described the first preparation of "$\gamma$-homocholine."[16] Partheil[17] in 1892 reported that he could not repeat Weisz's work but that he had synthesized "$\gamma$-homocholine" by a modification of Weisz's method. He also synthesized "$\gamma$-homocholine" in two other ways.[18] The first method may be represented schematically as follows

$$(CH_3)_3N(I)CH_2CH{=}CH_2 + HI \longrightarrow (CH_3)_3NICH_2CH_2CH_2I \xrightarrow[\text{aqueous}]{AgNO_3}$$

$$(CH_3)_3N(NO_3)CH_2CH_2CH_2OH \xrightarrow{HCl} (CH_3)_3N(Cl)CH_2CH_2CH_2OH$$

This "$\gamma$-homocholine" corresponded in properties to that which he synthesized by his modification of Weisz's method. Partheil synthesized a "$\gamma$-homocholine" which had different properties than his first one by the condensation of a solution of trimethylamine in alcohol with trimethylene chlorohydrin.[19] The chloroaurate of this compound melted at 180°.

In 1910 Malengreau and Lebailly[20] also condensed a solution of tri-

[12] Berlin, *Z. Biol.*, **57**, 15, 24 (1911).
[13] Partheil, *Ann.*, **268**, 176 (1892).
[14] Niemilowicz, *Monatsh.*, **7**, 241 (1886).
[15] Menge, *J. Biol. Chem.*, **10**, 401 (1911).
[16] Weisz, *Z. Naturwissenschaft*, **60**, 275 (1887).
[17] Partheil, *Ann.*, **269**, 179 (1892).
[18] Partheil, *ibid.*, **268**, 169 (1892).
[19] Partheil, *ibid.*, **268**, 184 (1892).
[20] Malengreau and Lebailly, *Z. physiol. Chem.*, **67**, 39 (1910).

methylamine in alcohol with trimethylene chlorohydrin. The chloroaurate of their "γ-homocholine" melted at 183°.

The next year Berlin[21] reported that he had also carried out the same condensation but that not only was "γ-homocholine chloride" formed but that a less soluble fraction could be isolated from the products of the reaction. He stated that this less soluble portion contained the ether of "γ-homocholine chloride." The chloroaurate of his "γ-homocholine" melted at 193–194°.

Berlin also reported that Zinnius[22] in 1910 had described the condensation of hypochlorous acid with trimethylallylammonium chloride. Apparently he obtained a mixture of $(CH_3)_3N(Cl)CH_2CH(OH)CH_2Cl$ and of $(CH_3)_3N(Cl)CH_2CH(Cl)CH_2OH$. One of these compounds could not be reduced satisfactorily by zinc and sulfuric acid. The other, which probably had the formula $(CH_3)_3N(Cl)CH_2CH(Cl)CH_2OH$, was reduced to a homocholine the choroaurate of which melted at 194° and which corresponded apparently in every way with Berlin's "γ-homocholine."

Berlin also obtained some "γ-homocholine" alone with some "β-methylcholine" by a condensation between methyl iodide, sodium alcoholate and a mixture of 1-hydroxy-3-aminopropane and of 1-amino-2-hydroxypropane.

In 1916 von Braun[23] synthesized a "γ-homocholine" whose chloroaurate melted at 193° and which corresponded very closely to that made by Berlin.

We have made γ-homocholine by the condensation of a solution of trimethylamine in benzene with trimethylene chlorohydrin. The properties of this γ-homocholine corresponded very closely to those of the "γ-homocholine" obtained by von Braun[23] and by Berlin.[24] We did not obtain any of the ether of γ-homocholine that Berlin found but this may be due to the fact that we used a solution of trimethylamine in benzene rather than in alcohol as he did. We found that in general a solution of trimethylamine in alcohol was not as satisfactory for most of these reactions as one in benzene since there was a greater tendency for the alkyl halide to dissociate in alcohol and for trimethylamine hydrohalide to be formed.

We have also attempted to repeat the preparation of the "γ-homocholine" that was obtained by Partheil[25] by the action of an aqueous solution of silver nitrate on "trimethyl-γ-iodopropylammonium iodide." Instead of obtaining, as he reported, a "γ-homocholine" whose chloroaurate melted at 162–164°, we obtained a mixture of true β-methylcholine and of ammonium salts.

[21] Berlin, *Z. Biol.*, **57**, 20 (1911).
[22] Zinnius, Marburg Dissertation, 1910; Berlin, *Z. Biol.*, **57**, 10 (1911).
[23] Von Braun, *Ber.*, **49**, 970 (1916).
[24] Berlin, *Z. Biol.*, **57**, 18 (1911).
[25] Partheil, *Ann.*, **268**, 175 (1892).

## Experimental Part

**Preparation of Ethyl α-Dimethylaminopropionate,** $CH_3CHN(CH_3)_2COOC_2H_5$.—A 33⅓% solution of dimethylamine in absolute alcohol was added in small portions to a solution of 100 g. of ethyl α-bromopropionate in 300 cc. of dry ether. The mixture was at first cooled in ice and then allowed to stand in a warm place (35°) overnight. The dimethylamine hydrobromide which precipitated was filtered off and the ethereal solution extracted with cold dilute sodium hydroxide. The ethereal layer was separated and dried over anhydrous sodium sulfate. This solution was then distilled. The fraction, b. p. 154–157° at 759 mm., was collected.[26] The ester was a colorless liquid with a slightly ammoniacal odor; yield, 57%.

**Preparation of Trimethylacetonylammonium Chloride,** $(CH_3)_3N(Cl)CH_2COCH_3$.—To 10 g. of monochloroacetone was added in small portions a slight excess of a 33% solution of trimethylamine in benzene. The temperature of the mixture was maintained at 0° until the reaction was complete. The product was collected and purified by dissolving it in absolute alcohol and reprecipitating it with dry ether. Trimethylacetonylammonium chloride was obtained in the form of white hygroscopic needle-like crystals, soluble in water and alcohol but insoluble in ether, m. p. 140°; yield, 80%.

*Anal.* Calcd. for $C_6H_{14}ONCl$: N, 9.27; Cl, 23.40. Found: N, 9.57, 9.63; Cl, 23.30.

The properties of the chloroplatinate, m. p. 238–240°, and chloroaurate, m. p. 139.5°, corresponded with those ascribed to them by Niemilowicz.[27]

**Reduction of Trimethylacetonylammonium Chloride.**—Five grams of trimethylacetonylammonium chloride in 25 cc. of absolute alcohol was catalytically reduced in the presence of 0.1 g. of platinum oxide (Adams) and one drop of a normal solution of ferric chloride in water. After the theoretical amount of hydrogen had been absorbed the solution was filtered from platinum and all the alcohol evaporated *in vacuo*. The oil that remained was kept in a vacuum desiccator for three days, during which time it all crystallized. The solid was dissolved in absolute alcohol which had previously been saturated with hydrogen sulfide. The small amount of iron sulfide which precipitated was removed by shaking the solution with activated charcoal. β-Methylcholine chloride was precipitated as an oil from the filtrate of the mixture by the addition of dry ether. The ether layer was decanted and the oil repeatedly washed with small portions of dry ether until crystallization started. The product was further purified by recrystallization from a small amount of butyl alcohol. It appeared in the form of white hygroscopic needles, soluble in water and alcohol but insoluble in ether; m. p. 165°; yield, 50%.

*Anal.* Calcd. for $C_6H_{16}ONCl$: N, 9.13; Cl, 23.10. Found: N, 9.23, 9.37; Cl, 23.15.

The properties of the chloroplatinate, m. p. 257° with decomposition, and the chloroaurate, m. p. 196°, of this β-methylcholine corresponded very closely to those ascribed by Menge[15] to the corresponding salts of "α-methylcholine."

**Preparation of β-Methylcholine Chloride and γ-Homocholine Chloride.**—A mixture of 15 g. of the appropriate chlorohydrin, propylene chlorohydrin, b. p. 125–128° for the preparation of β-methylcholine chloride, and trimethylene chlorohydrin for γ-homocholine chloride, and a slight excess of a 33% solution of trimethylamine in benzene was heated in a sealed tube at 100° for eight hours. The reaction product was dissolved in a small amount of warm absolute alcohol and the solution decolorized with

[26] Karrer, Ref. 8, gives 154° at 740 mm. as the b. p. of ethyl α-dimethylaminopropionate.

[27] Niemilowicz, *Monatsh.*, **7**, 241 (1886).

activated charcoal. Dry ether was added to the filtrate from this mixture. The precipitate was washed with small portions of dry ether. White needle-like crystals were obtained which were soluble in alcohol and water but insoluble in ether.

**β-Methylcholine chloride** was further purified by recrystallization from butyl alcohol; yield, 48%; m. p. 165°. The melting point of a mixture of this compound with the β-methylcholine chloride obtained by the reduction of trimethylacetonylammonium chloride also melted at 165°.

*Anal.* Calcd. for $C_6H_{16}ONCl$: N, 9.13. Found: N, 9.18. *Chloroplatinate:* Calcd. for $C_{12}H_{32}O_2N_2PtCl_6$: Pt, 30.22. Found: Pt, 30.28. *Chloroaurate:* Calcd. for $C_6H_{16}ONAuCl_4$: Au, 43.07. Found: Au, 43.12.

The melting points of mixtures of the chloroplatinate, m. p. 257°, and the chloroaurate, m. p. 196°, of this β-methylcholine with the corresponding salts of the β-methylcholine formed by the reduction of trimethylacetonylammonium chloride were the same as those of the constituents of the mixtures.

**β-Methylcholine Picrate.**—A slight excess of the theoretical amount of silver oxide was shaken with a solution of 1 g. of β-methylcholine chloride (obtained by the action of trimethylamine on propylene chlorohydrin) in 10 cc. of water. The temperature was kept at 0° in order to prevent the formation of trimethylamine. Silver chloride and the excess of silver oxide were filtered off and the calculated amount of a solution of picric acid in absolute alcohol was added to the filtrate. The solution was evaporated to a small volume on the steam-bath. When absolute alcohol was added to the residue and the solution cooled, yellow needle-like crystals were precipitated; m. p. 163°.[28]

*Anal.* Calcd. for $C_{12}H_{18}O_8N_4$: N, 16.18. Found: N, 16.00, 16.32.

**γ-Homocholine chloride** melted at 173°; yield, 92%.

*Anal.* Calcd. for $C_6H_{16}ONCl$: C, 46.80; H, 10.40; Cl, 23.15. Found: C, 46.51; H, 10.13; Cl, 23.00.

TABLE I

ESTERS OF α- AND β-METHYLCHOLINE CHLORIDE AND γ-HOMOCHOLINE CHLORIDE

| No. | Choline chloride | Anhydride | Hours heated | M. p., °C., of ester | Yield, % |
|---|---|---|---|---|---|
| 1 | α-Methyl-[a] | Acetic | 12 | 152–154 | .. |
| 2 | β-Methyl-[b] | Acetic | 6 | 172–173 | .. |
| 3 | β-Methyl-[c] | Acetic | 6 | 172–173[d] | 80 |
| 4 | β-Methyl-[c] | Propionic | 3 | ..... | .. |
| 5 | γ-Homo- | Acetic | 6 | 142–143 | 80 |

| No. | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Nitrogen, % Calcd. | Nitrogen, % Found | Chlorine, % Calcd. | Chlorine, % Found |
|---|---|---|---|---|---|---|---|---|
| 1 | ... | ... | .. | .. | 7.17 | 7.01 | 18.15 | 18.32 |
| 2 | ... | ... | .. | .. | .. | .. | 18.15 | 17.93 |
| 3 | 49.00 | 49.14 | 9.20 | 9.29 | .. | .. | 18.15 | 17.97 |
| 4 | ... | ... | .. | .. | 6.68 | 6.54 | ... | ... |
| 5 | ... | ... | .. | .. | 7.17 | 6.99 | 18.15 | 18.18 |

[a] Prepared by the method of Karrer, Ref. 8. [b] Prepared by the reduction of trimethylacetonylammonium chloride. [c] Prepared by the action of propylene chlorohydrin upon trimethylamine. [d] A mixture of this acetyl-β-methylcholine chloride with that obtained by the acetylation of the β-methylcholine chloride obtained by the reduction of trimethylacetonylammonium chloride also melted at 172–173°.

[28] The picrate of the β-methylcholine which was obtained by the reduction of trimethylacetonylammonium chloride also melted at 163° as did a mixture of the two picrates.

The properties of the chloroaurate, m. p. 193°, and the chloroplatinate, m. p. 237°, of this γ-homocholine chloride were the same as those ascribed to these compounds by Berlin[21] and by von Braun.[23]

**Acylation of α- and β-Methylcholine Chloride and of γ-Homocholine Chloride.**—The three homologs of choline chloride were acylated by heating a mixture of one molecular portion of the homo- or methylcholine with seven molecular portions of the acid anhydride at 100°. After the acylation was complete dry ether was added to the cooled solution. The precipitate was washed several times with ether and then dissolved in absolute alcohol. This solution was first decolorized with activated charcoal and then the acylated compound reprecipitated by the addition of dry ether. The products were white hygroscopic solids which were readily soluble in water.

**Attempted Preparation of Partheil's "γ-Homocholine."**—The equivalent amount of silver nitrate in 300 cc. of water was added to 25 g. of trimethyliodopropylammonium iodide.[29] The precipitated silver iodide was filtered off and a second equivalent of silver nitrate added to the filtrate. The mixture was placed in a blackened flask and heated on a steam-bath. During the course of the reaction the precipitated silver iodide was removed from time to time until no more of it was formed (five days). Sufficient dilute hydrochloric acid was then added to precipitate the small amount of silver nitrate that remained. The silver chloride was removed and the solution evaporated in a vacuum desiccator over calcium chloride and solid sodium hydroxide. When the solution reached a volume of 150 cc. it was saturated with hydrogen sulfide to remove the small amount of silver salts still in solution. The silver sulfide was removed by shaking the solution with activated charcoal and the hydrogen sulfide removed by boiling *in vacuo*. Dilute hydrochloric acid and platinic chloride in excess were now added to the filtrate from this mixture. A small amount of precipitate was obtained which increased in amount if the reaction between the silver nitrate and the trimethyliodopropylammonium nitrate continued for a longer time than five days.

This precipitate was recrystallized several times from water which contained a little hydrochloric acid. It was obtained finally in the form of yellow regular crystals almost insoluble in cold water and but slightly soluble in boiling water; m. p. above 300°. The odor of ammonia was detected when caustic alkali was added to this solid.

*Anal.* Calcd. for $(NH_4)_2PtCl_6$: Pt, 44.00. Found: Pt, 43.80.

Alcohol was added to the filtrate from which the ammonium chloroplatinate was originally separated. A precipitate formed which was recrystallized several times from water containing a small amount of dilute hydrochloric acid. A chloroplatinate which melted at 257° was obtained. This corresponded with β-methylcholine chloroplatinate and not with γ-homocholine chloroplatinate which melts at 237°.

*Anal.* Calcd. for $C_{12}H_{32}O_2N_2Cl_6Pt$: Pt, 30.22. Found: Pt, 30.41, 30.44.

A small portion of this chloroplatinate was dissolved in water and the solution was saturated with hydrogen sulfide. Platinic sulfide was removed by filtration and the filtrate evaporated to dryness *in vacuo* (20 mm.). The oil which remained was dissolved in water and a small amount of platinic sulfide removed with activated charcoal. The solution was boiled *in vacuo* to remove a slight amount of hydrogen sulfide and auric chloride was then added in slight excess. β-Methylcholine chloroaurate which was slightly impure was obtained. Upon repeated recrystallization it appeared in the form of golden yellow leaflets; m. p. 196°. The melting point of a mixture of this chloroaurate with pure β-methylcholine chloroaurate remained at 196°. The compound, however, was slightly impure as it sintered at a temperature of 180° although it did not melt until 196°. Evidently the amount of contaminating material was slight or con-

[29] Prepared according to the method of Partheil, Ref. 18.

sisted of an isomeric substance since it was not noticeable analytically. Possibly ammonium chloroaurate which is less soluble than the chloroaurate of β-methylcholine persisted in spite of the many recrystallizations.

*Anal.* Calcd. for $C_6H_{16}ONCl_4Au$: Au, 43.07. Found: Au, 43.15, 43.08.

The authors wish to express their appreciation to Mr. Douglass F. Hayman for most of the analyses which are recorded in this paper.

## Summary

1. It has been shown that the only true α-methylcholine that has ever been made was that made by Karrer.[8]

2. True β-methylcholine chloride has been prepared by the reduction of trimethylacetonylammonium chloride.

3. It has been shown that β-methylcholine chloride may be obtained by the condensation of propylene chlorohydrin and trimethylamine.

4. γ-Homocholine chloride has been obtained by the condensation of trimethylene chlorohydrin with a solution of trimethylamine in benzene.

5. We have repeated the process used by Partheil to make his "γ-homocholine," the chloroaurate of which melted at 162°. We were not able to isolate any of the salts of γ-homocholine from the reaction mixture but have found salts of ammonia and of β-methylcholine in it.

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

# OPTICAL CRYSTALLOGRAPHIC DATA FOR SOME SALTS OF STRYCHNINE

BY CHARLES F. POE AND JESSE E. SELLERS

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## Introduction and Historical

The literature reveals that very few optical data have been reported for the salts of strychnine. Some of these are reported by Groth[1] and Bolland[2] and include two of the refractive indices for the nitrate and the hydroiodide and one for the sulfate. Several investigators have studied the optical properties of other alkaloids, usually the bases themselves. Wherry and Yanovsky[3] made such measurements for the cinchona alkaloids. Other investigators along these lines include Kley,[4] Wright,[5] Wherry,[6] and Keenan.[7]

[1] Groth, "Chemische Krystallographie," 1906–1919.

[2] Bolland, *Monatsh.*, **31**, 387 (1910).

[3] Wherry and Yanovsky, THIS JOURNAL, **40**, 1063 (1918).

[4] Kley, *Z. anal. Chem.*, **43**, 160 (1904).

[5] Wright, THIS JOURNAL, **38**, 1647 (1916).

[6] Wherry, *U. S. Dept. of Agric. Bull.*, 679 (1918).

[7] Keenan, *J. Am. Pharm. Assoc.*, **16**, 837 (1927).

This paper describes a number of salts of strychnine which were prepared for the purpose of perfecting a method for the micro-chemical detection of strychnine and gives the optical crystallographic data concerning them.

**Preparation of Salts.**—With the exception of the chlorate and thiocyanate, the salts were all prepared in a similar manner. Molecular quantities of strychnine and the acid were mixed, and water added. The solutions were then heated for several minutes, filtered and the salt was allowed to crystallize. The salt was then recrystallized until pure. Except in cases where water of crystallization would be given off, the salts were dried in the air. The chlorate and thiocyanate were prepared by dissolving the alkaloid in very dilute acetic acid and adding solutions of equivalent quantities of potassium chlorate or potassium thiocyanate.

**Analysis of the Salts.**—Each salt was analyzed for the percentage of strychnine by the picric acid method.[8] The strychnine content was determined on each salt containing water of crystallization and on the anhydrous salt. Nitrogen was determined by the Kjeldahl–Gunning–Arnold method and water of crystallization in each compound was estimated by drying over sulfuric acid, phosphorus pentoxide, or by heating the salt. The water of crystallization in all cases was also determined by the Germann and Muench[9] modification of Wilson's[10] vapor pressure method. It was found difficult to get the balance air-tight enough for atmospheres of low or high aqueous tension. In order to avoid this difficulty, a modification of the method was worked out. A square bottle was placed on its side in the balance case with the large mouth pointing outward. The opening of the bottle was covered with a glass plate, ground to fit, and sealed with vaseline. A hole was drilled in the upper side of the bottle through which the pan support of the balance passed. The cover glass containing the sample was placed on this pan. The same concentration of acid was used both inside the bottle and in the balance case. The balance case doors were closed and made as air-tight as possible by caulking with cotton-wool.

The compounds prepared and studied, together with their analyses, appear in Table I. Of the salts reported in Table I, the methods for preparation of the disuccinate, glutarate, maleate, chlorate and the thiocyanate[11] were not found in the literature. The malonate, dioxalate and selenate were each found to contain an amount of water of crystallization different from that previously reported.

[8] Elmore, *J. Assoc. Off. Agric. Chem.*, **9**, 224 (1926).

[9] Germann and Muench, *J. phys. Chem.*, **32**, 1380 (1928).

[10] Wilson, THIS JOURNAL, **43**, 704 (1921).

[11] Dollfus, *Ann. Chem. Pharm.*, **65**, 221 (1848), describes a compound supposed to be the thiocyanate, but the analysis given does not correspond to the present formula for this salt.

TABLE I

SALTS OF STRYCHNINE

| Salt of strychnine | Formula S = $C_{21}H_{22}O_2N_2$ | Strychnine, %, in hydrated salt Calcd. | Found | Strychnine, %, in anhydrous salt Calcd. | Found | Nitrogen, % Calcd. | Found | Water of crystallization found % | No. of molecules | Possible no. of molecules of water by vapor pressure method |
|---|---|---|---|---|---|---|---|---|---|---|
| Dioxalate | $S \cdot C_2H_2O_4 \cdot 1.5H_2O$ | 74.07 | 74.07 | 78.79 | 78.66 | 6.20 | 6.20 | 5.79 | 1.45 | 1.5 |
| Disuccinate | $S \cdot C_4H_6O_4 \cdot H_2O$ | 71.07 | 71.15 | 73.90 | 73.71 | 5.95 | 5.97 | 3.83 | 1.00 | 1.0 |
| Ditartrate | $S \cdot C_4H_6O_6 \cdot 3H_2O$ | 62.09 | 62.26 | 69.02 | 69.46 | 5.20 | 5.17 | 9.88 | 2.95 | 3.0 |
| Chlorate | $S \cdot HClO_3 \cdot H_2O$ | 76.54 | 76.58 | 79.83 | 80.04 | 6.42 | 6.33 | 4.13 | 1.00 | 1.0 |
| Glutarate | $S \cdot C_5H_8O_4$ | 71.68 | 71.85 | 71.68 | 71.85 | 6.00 | 5.92 | None | None | None |
| Hydrobromide | $S \cdot HBr \cdot H_2O$ | 77.17 | 77.42 | 80.51 | 80.08 | 6.46 | 6.48 | 3.87 | 0.93 | 1.0 |
| Hydrochloride | $S \cdot HCl \cdot 1.75H_2O$ | 83.09 | 83.24 | 90.17 | 90.24 | 6.96 (Cl, 8.82) | 6.99 (Cl, 8.86) | 3.27 | 1.73 | 1.75 |
| Hydroiodide | $S \cdot HI \cdot H_2O$ | 69.61 | 69.63 | 72.32 | 71.99 | 5.83 | 5.82 | 3.75 | 1.00 | 1.0 |
| Maleate | $S \cdot C_4H_4O_4 \cdot H_2O$ | 71.38 | 71.19 | 74.23 | 74.24 | 5.98 | 6.11 | 4.36 | 1.13 | 1.00 |
| Malonate | $S_2 \cdot C_3H_3O_4 \cdot 6H_2O$ | 75.91 | 75.57 | 86.53 | 86.28 | 6.36 | 6.28 | 12.09 | 5.90 | 6.0, 3.0 |
| Nitrate | $S \cdot HNO_3$ | 84.14 | 84.24 | 84.14 | 84.24 | 10.57 | 10.43 | None | None | None |
| Oxalate | $S_2 \cdot C_2H_2O_4 \cdot 4.5H_2O$ | 79.62 | 79.79 | 88.14 | 88.17 | 6.67 | 6.74 | 9.26 | 4.33 | 4.5, 4.0, 2.0 |
| Perchlorate | $S \cdot HClO_4 \cdot H_2O$ | 73.83 | 73.94 | 76.89 | 76.58 | 6.18 | 6.11 | 3.98 | 1.00 | 1.0 |
| Phosphate | $S \cdot H_3PO_3 \cdot 2H_2O$ | 71.36 | 71.40 | 77.32 | 77.51 | 5.98 | 6.14 | 7.60 | 1.97 | 2.0 |
| Selenate | $S_2 \cdot H_2SeO_4 \cdot 4.5H_2O$ | 74.71 | 74.61 | 82.16 | 82.08 | 6.26 | 6.20 | 8.96 | 4.45 | 5.0(?), 4.5, 2.0 |
| Sulfate | $S_2 \cdot H_2SO_4 \cdot 5H_2O$ | 78.03 | 78.03 | 87.20 | 86.83 | 6.54 | 6.61 | 10.55 | 5.02 | 6.0, 5.0 |
| Sulfate | $S_2 \cdot H_2SO_4 \cdot 6H_2O$ | 76.42 | 76.04 | 87.20 | 86.83 | 6.40 | 6.44 | 12.25 | 5.94 | 6.0, 5.0 |
| Thiocyanate | $S \cdot HCNS \cdot H_2O$ | 81.26 | 81.24 | 84.98 | 85.30 | 10.22 | 10.31 | 4.76 | 1.09 | 1.0 |

TABLE II

OPTICAL CRYSTALLOGRAPHIC DATA FOR SOME SALTS OF STRYCHNINE[a]

All salts biaxial except the uniaxial malonate

| Strychnine salt | Habit | Optical character (sign) | Sign of elongation | Refractive indices 25° $\alpha$ | $\beta$ | $\gamma$ | 2 V-Dispersion | Crystal system |
|---|---|---|---|---|---|---|---|---|
| Dioxalate, $1.5H_2O$ | Stout needles | + | ± usually − | 1.592 | 1.603 | 1.665 | Large, $\rho > v$ | Monoclinic, ext. angle = 69.5° |
| Disuccinate, $H_2O$ | Needles | − | − | 1.588 | 1.646 ± | 1.662 | Large | Orthorhombic ? |
| Ditartrate, $3H_2O$ | Stout needles | + | Indeterm. | 1.596 | 1.603 | 1.632 | Large, marked, $\rho > v$ | Monoclinic |
| Chlorate, $H_2O$ | Fine needles | + | − | 1.605 | 1.611 | 1.663 | Moderate, horizontal | Monoclinic $x = b$ |
| Glutarate | Needles | − | − | 1.575 | | 1.655 | | |
| Hydrobromide, $H_2O$ | Needles | + | − | 1.646 | 1.650 | 1.73 ± | Small, weak | Monoclinic |
| Hydrochloride, $1.75H_2O$ | Fine needles | + | − | 1.609 | 1.627 | 1.662 | Large, weak, $\rho > v$ | Orthorhombic |
| Hydroiodide, $H_2O$ | Stout needles | + | − | 1.661 (1.66) | 1.665 | 1.73 ± (1.69) | Small, $\rho > v$ | Monoclinic |
| Maleate, $H_2O$ | Rods | − ? | − | 1.544 | 1.598 | 1.667 | Large | Orthorhombic |
| Malonate, $6H_2O$ | Plates | − | | $\epsilon$ = 1.608 | $\omega$ = 1.610 | | | Tetragonal |
| Nitrate | Fine needles | + | − | 1.610 (1.62) | 1.624 | 1.675 (1.67) | Large, $\rho > v$ | Monoclinic |
| Oxalate, $4.5H_2O$ | Needles | + | ± | 1.592 ± | 1.598 | 1.662 | Small, $\rho > v$ | Monoclinic |
| Perchlorate, $H_2O$ | Stout needles | + | ± | 1.589 | 1.598 | 1.654 | Moderate, inclined | Monoclinic, ext. angle = 22° |
| Phosphate, $2H_2O$ | Needles | + | ± | 1.589 | 1.597 | 1.655 | Moderate, inclined | Monoclinic $y = b$ |
| Selenate, $4.5H_2O$ | Stout needles | + (+) | − | 1.598 | 1.600 | 1.661 | Small, $\rho < v$, $2E$ = 10° ($\rho < v$, $2E$ = 14°) | Monoclinic |
| Sulfate, $5H_2O$ | Stout needles | + (+) | − | 1.592 | 1.597 | 1.661 (1.594) | Small, weak, $2E$ = 16° ($2E$ = 16°31′) | Monoclinic |
| Sulfate, $6H_2O$ | Plates | − (−) | | 1.595 | 1.613 | 1.615 | Small $2E$ up to 30° | Orthorhombic or pseudotetragonal |
| Thiocyanate, $H_2O$ | Stout needles | + | ± | 1.651 | 1.654 | 1.695 | Small, inclined | Monoclinic, $y = b$ |

[a] All values in the table enclosed in parentheses are those previously reported in the literature.

**Optical Crystallographic Data.**—The optical crystallographic data were obtained for each of the salts reported in Table I. The methods used were those described in the texts by Chamot and Mason,[12] by Winchell,[13] and by various other books on optical mineralogy. The refractive indices were determined by the immersion method using daylight obtained from the northern sky. At times it was very difficult to get the crystals to stand on end so as to permit the measurement of a third refractive index. In such cases, finely ground glass-wool was mixed with the crystals and its particles held a sufficient number in upright position. The values for $2V$ were determined from the curvature of the isogyre in a centered optic axis interference figure or, in case of the smaller angles, by measuring the distance between the optic axes with an eyepiece micrometer, calibrated against a mineral of a known axial angle. The determination of this angle is not extremely accurate, therefore, the values for $2V$ are reported in the table as large, moderate or small. The extinction angle was determined by turning the crystal to extinction and measuring the angle between this position and the long edge of the crystal. The refractive indices, together with other optical data, are given in Table II.

## Summary

1. Five new salts of strychnine have been prepared and described.

2. The data in the literature concerning thirteen salts of strychnine have been redetermined, and corrections have been made in the water of crystallization for the dioxalate, malonate and the selenate.

3. The anhydride for each salt was prepared and analyzed.

4. The optical crystallographic data for eighteen salts of strychnine have been determined.

BOULDER, COLORADO

[12] Chamot and Mason, "Handbook of Chemical Microscopy," John Wiley and Sons, Inc., New York, 1930.

[13] Winchell, "Elements of Optical Mineralogy," John Wiley and Sons, Inc., New York. 1928.

[CONTRIBUTION FROM THE DEPARTMENT OF ZOÖLOGY, UNIVERSITY OF WISCONSIN]

# HORMONES OF THE CORPUS LUTEUM. THE SEPARATION AND PURIFICATION OF THREE ACTIVE SUBSTANCES[1]

BY H. L. FEVOLD, F. L. HISAW AND S. L. LEONARD

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We have previously reported the extraction and separation of two active principles from the corpora lutea of the sow.[2] One of these was called relaxin due to its ability to cause relaxation of the pelvic ligaments. The second fraction, from which the relaxin had been eliminated, was physiologically active in producing several reactions ordinarily attributed to the corpora lutea, such as mucification of the vaginal mucosa of rats, production of a premenstrual endometrium in monkeys, development of the pseudopregnancy picture in the uterus of rabbits and growth of deciduomata in the uterus of castrate rats and guinea pigs.

We were at that time of the opinion that all these reactions, other than relaxation of the pelvic ligaments, were caused by the same active principle. At the present time, however, we have been able to separate from this fraction two substances, one of which produces the mucification reaction, while the second produces the premenstrual endometrium in monkeys, the pseudopregnancy picture in the rabbit's uterus, and deciduomata. We have, therefore, three hormones elaborated by the corpora lutea of the sow: *relaxin*, which has a specific action on the pelvic ligaments, *corporin*, which is concerned with the physiology of the uterus, while the mucifying principle acts on the vaginal mucosa.[3]

**Methods of Testing.**—Early workers almost invariably used inhibition of ovulation as a criterion for the potency of corpus luteum preparations. This end-point has been shown to be unreliable and this fact led to the confusion which existed for some time. However, in recent years several reliable physiological tests have been worked out by investigators in the field of endocrinology. One of these is the relaxation reaction used by Hisaw for the relaxative hormone.[4] The basis for other tests is the production of definite histological pictures in the uterus and vagina of various laboratory animals characteristic of the changes which normally occur during pregnancy or in the oestrous cycle when the corpora lutea of the ovary

[1] This work has been assisted by grants from the Committee for Research of Sex of the National Research Council and by the University of Wisconsin Research Funds.

[2] H. L. Fevold, F. L. Hisaw and R. K. Meyer, *Proc. Soc. Exptl. Biol. Med.*, **27**, 604, 606 (1930).

[3] The non-identity of the mucifying principle and the substance responsible for progestational development, etc., has also been recognized by Dr. R. K. Meyer and W. M. Allen, Rochester Medical School, Rochester, N. Y. They have also separated the two hormones from each other using the same general principles discussed here.

[4] F. L. Hisaw, *Anat. Rec.*, **37**, 126 (1927); *Phys. Zoölogy*, **2**, 59 (1929).

are functional. Four of these histological changes which may be used as physiological end-points in a chemical study are as follows: the production of placentomata;[5] the mucification of the vaginal mucosa of rats;[6] the production of the pseudopregnancy picture in the uterus of rabbits;[7] and the production of a premenstrual endometrium in the uterus of monkeys.[8]

All of these tests have been used in our laboratory and it has been definitely shown that these reactions are not all due to the same chemical substance. Relaxation of the pelvic ligaments is produced by relaxin, which does not produce any of the other four reactions named above. The pseudopregnancy reaction in the rabbit and the premenstrual picture in the monkey is produced by a second hormone which we named *corporin* and which Corner calls *progestin*,[7] while the mucification of the vaginal mucosa is due to a third separate principle which may be called the mucifying hormone. These three hormones have been separated from one another after being obtained in extract form by means of acid alcohol.

The activities of the corpus luteum hormones are measured in guinea pig units for relaxin, rat units for the mucifying hormone and rabbit units for corporin. The guinea pig unit for the relaxative hormone has already been described.[9] A rabbit unit of corporin is that amount of the active substance which brings about a very good pseudopregnancy picture in the rabbit's uterus when injected over a period of four days following castration of the rabbit in heat. The picture thus produced corresponds to that designated as + + + + by Corner. A rat unit of the mucifying hormone is that amount of the hormone which brings about a mucified condition of rats' vaginas similar to that of a six or seven day pseudopregnancy when injected over a period of four days following castration in full oestrum and killed on the fifth day.

**General Methods of Extraction.**—The corpus luteum hormones are extracted from fresh sow corpora lutea by means of acidified 95% alcohol (20 cc. concd. HCl per liter). This solvent is more efficient in extracting the active principles than any other which we have used and the hormones may later be separated from one another quite readily. Corporin and the vacuolating hormone may be extracted from the tissue by means of neutral alcohol, but in this case little or none of the relaxin is obtained and the yield of the vacuolating hormone is reduced. This procedure is, therefore, not advantageous and complicates the process for the removal of the hormones. It is, however, possible to obtain a fairly complete separation

[5] C. K. Weichert, *Proc. Soc. Exptl. Biol. Med.*, **25**, 490 (1928); L. A. Goldstein and A. J. Tatelbaum, *Am. J. Phys.*, **91**, 14 (1929).

[6] R. K. Meyer, unpublished.

[7] G. W. Corner and W. M. Allen, *ibid.*, **88**, 326 (1929).

[8] F. L. Hisaw, R. K. Meyer and H. L. Fevold, *Proc. Soc. Exptl. Biol. Med.*, **27**, 400 (1930).

[9] H. L. Fevold, F. L. Hisaw and R. K. Meyer, THIS JOURNAL, **52**, 3340 (1930).

of relaxin from the other two hormones by this method. After extraction with neutral alcohol, the tissue is extracted for relaxin and purified as previously described.

The yield of corporin can be increased by extracting the tissue by means of hot acid alcohol. The presence of acid aids materially in this extraction due to the fact that during the process the tissue is disintegrated to a fine pulp, allowing a very efficient extraction of the active material. The yield of the vacuolating hormone is, however, not increased by this method and the relaxin is destroyed completely due to its lability toward heat. This method, therefore, can be used only when corporin and the vacuolating hormone are the active principles desired or a hot acid–alcohol extraction may be carried out on the residue after the cold extractions.

The separation of the three hormones has been made possible by their different solubilities in alcohol and ether. Relaxin is first separated from corporin and the mucifying principle due to the fact that it is insoluble in absolute (99%) alcohol while the other two are soluble in this medium. Corporin is also soluble in ether, acetone or petroleum ether whereas the mucifying hormone is insoluble in ether and petroleum ether and only slightly soluble in acetone. The character of these three hormones varies, therefore, from a substance which is probably peptide-like in nature to a substance which has the solubilities of a fat-like substance.

**General Characteristics of Corporin and the Mucifying Hormone.**— Corporin is extracted from the corpus luteum tissue by methods already described and is purified by the elimination of proteins and their degradation products, phospholipins, fatty acids, neutral fats and cholesterol with the result that a preparation is obtained which is active in very small amounts in producing the characteristic reaction. The active material is sparingly soluble in water, quite soluble in ether and petroleum ether, but more soluble in methyl and ethyl alcohol. It is soluble in benzene, acetone, pyridine and other organic solvents. It is stable toward dilute acids even at boiling temperatures but very unstable toward alkalies above a $P_H$ of 9. It is also readily destroyed by oxidation, even by air at room temperature.

The mucifying hormone differs from corporin in many of its characteristics, its main difference being that it is not appreciably soluble in fat solvents such as ethyl ether, petroleum ether or benzene. This difference of solubility has enabled us to separate the two hormones from each other. It is, however, readily soluble in methyl or ethyl alcohol, pyridine and acetic acid, but more difficultly soluble in acetone. It is also readily soluble in distilled water. It is especially soluble in aqueous media above a $P_H$ of 7, while in acidified solution a clear, stable colloidal solution is obtained.

The hormone is relatively stable as compared to relaxin and corporin. However, it is similar to these two in that it is unstable toward alkalies.

In alkaline solution above $P_H$ 9.5 its activity is slowly destroyed while in more concentrated alkaline solution decrease of activity takes place rapidly. Acidified alcoholic or aqueous solutions are quite stable. Boiling such solutions for short periods seems to have no effect on their activity. Oxidation in aqueous solution with hydrogen peroxide or dilute nitric acid does not destroy the active principle. Formaldehyde, however, inactivates the preparation completely, as does also acetyl or benzoyl chloride and nitrous acid. It is not injured by tryptic or peptic digestion. It is not precipitated by picric, trichloroacetic or tannic acid nor have we been able to precipitate the active material by isoelectric precipitation. These points differentiate the mucifying factor from relaxin and indicate that it is not peptide-like in structure.

## Experimental

**Method of Extraction.**—The details of the preparation and properties of relaxin have been previously reported[9] so the following paper deals chiefly with corporin and the mucifying hormones. The separations of all three hormones must necessarily be given, however.

The corpora lutea used in these investigations have been obtained from the slaughter house as soon after the animals have been killed as possible. They are dissected from the ovaries, ground and covered with alcohol until they are to be extracted. The initial steps in the process are carried out in the same manner as given for relaxin. However, the first steps will be briefly given here. The procedure given below is typical for the extraction of one kilogram of corpus luteum tissue.

The corpora lutea are extracted twice at room temperature with two-liter portions of acidulated alcohol. The extracts are removed by pressing and the residual tissue is refluxed with one and one-half liters of acidulated alcohol for one hour. The extract is removed from the pasty residue and united to the first extracts. The residual tissue is discarded.

The united extracts are neutralized to $P_H$ of 6.8–7, filtered and the precipitate redissolved, reprecipitated and discarded. The neutralized extracts are evaporated to a thick paste under reduced pressure. During the course of this evaporation the solution foams strongly and it is practically impossible to accomplish the evaporation in the ordinary vacuum distillation set-up. We have made use of a special type of distillation flask designed by the Eastman Kodak Laboratories for frothing liquids.[10] The distillation from this type of flask presents no difficulties and very little attention is required during the course of the distillation. The temperature must not rise above 45–50°, since relaxin is decomposed quite rapidly above this temperature.

The thick paste which remains in the flask is then extracted with about 500 cc. of 95% alcohol. The residue is discarded while the alcoholic solution is again evaporated to dryness, emulsified in water and phospholipins eliminated by addition of one volume of acetone. The phospholipins are filtered off, the solution evaporated and again taken up in 95% alcohol.

The crude preparation which is thus obtained contains all three of the hormones of the corpus luteum. It contains about 1000 guinea pig units of relaxin, at least 125 rat units of the mucifying hormone and about 30 rabbit units of corporin. The next

[10] "Synthetic Organic Chemicals," Vol. IV, No. 2, 1930.

step in the procedure consists of the separation of relaxin from the other two hormones by means of absolute alcohol, relaxin being insoluble while corporin and the vacuolating hormone are readily soluble.

The alcoholic solution is evaporated to dryness and extracted with 250 cc. of 99% alcohol. The solution is allowed to stand for a few hours to permit the flocculent precipitate to settle out. The precipitate, which contains practically all of the relaxin, is centrifuged off, leaving the other hormones in solution. The purification of the relaxative hormone is then carried out as formerly described.[9]

Corporin and the mucifying hormone may then be separated from each other. This separation does not take place as smoothly and cleanly as does that of relaxin since in the presence of fats the mucifying hormone has a tendency to be somewhat soluble in ether. However, after the separation has been accomplished the mucifying hormone is insoluble or very slightly soluble in ethyl ether. Corporin on the other hand is readily soluble in this solvent and a separation can be effected.

The alcoholic solution is evaporated to small volume and 100 cc. of ethyl ether is added. A precipitate settles out which contains about 60 to 70% of the vacuolating hormone and very little or none of the corporin. The precipitate is centrifuged off and preserved in a little alcohol.

The ether solution is next evaporated to dryness and extracted with 100 cc. of dry ethyl ether. A second smaller precipitate is formed which is added to the first. This process is repeated until no more ether-insoluble material can be obtained. Approximately 90% of the mucifying hormone is obtained in the ether-insoluble material while the ether-soluble gives no reaction for this hormone. The separation is therefore practically complete. If any precipitate comes out when the ether-insoluble fraction is dissolved in 99% alcohol, it is centrifuged off and combined with the fraction containing the relaxin.

We have therefore at this point three preparations each containing one of three hormones elaborated by the corpora lutea of the sow, an alcohol-insoluble preparation containing relaxin, an alcohol-soluble but ether-insoluble fraction containing the mucifying hormone, and an alcohol-soluble and ether-soluble fraction containing corporin. The separation in each case is as complete as can be expected in work of this kind.

**Purification and Chemical Characteristics of the Mucifying Hormone.**—The absolute alcohol solution of the vacuolating hormone is treated with three volumes of ethyl ether. A precipitate is thrown down which is centrifuged off, redissolved in alcohol and reprecipitated with ether. The precipitate is inactive so is discarded. The ether–alcohol solution contains the active material. The solution is evaporated to dryness and dissolved in glacial acetic acid. To this solution are added three volumes of ethyl ether and a volume of petroleum ether equal to the combined volume of ethyl ether and glacial acetic acid. Brown drops of glacial acetic acid containing the active material gradually settle out. After standing for some time the concentrated glacial acetic acid is removed and the acetic acid evaporated in an air dryer.

The resulting preparation containing the active material is a golden brown substance which is very difficult to dry completely as it retains water and remains in a kind of gel-like condition. When dried down completely it is a brown substance of a rather waxy consistency. It is active in two-milligram doses injected daily for four days to a rat. It is best preserved in absolute alcohol. In such solution it has been kept for a year with no detectable decrease in activity.

The reaction of a few chemical agents on the active substance was investigated in an effort to obtain some knowledge about the possible nature of the active material itself. The preparation which we have obtained is undoubtedly still far from a pure substance and an elementary analysis of the material would show nothing as to the nature of the

hormone. However, some of the results reported below throw some light on the possible nature of the active molecule.

**Action of Alkalies.**—Three cc. of an active preparation containing fifteen rat units of hormone was adjusted to a $P_H$ of 9.5 by means of sodium hydroxide. This solution was allowed to stand for fifteen hours at room temperature. The solution was then neutralized, extracted with absolute alcohol and tested on a series of rats. Only about five rat units were recovered, showing a decided decrease in activity due to the presence of alkali.

The same experiment was repeated using alcoholic potash solution with similar results. The decrease in activity seemed to be slower in this case, however, as about eight to ten rat units were recovered at the end of twenty hours.

**Action of Formaldehyde.**—Ten cc. of the same solution as above containing 50 rat units was adjusted to $P_H$ of 4.5 and 5 cc. of formaldehyde solution was added. The solution was permitted to stand at room temperature for twenty hours. The formaldehyde was removed *in vacuo*, the residue extracted with ether and then taken up in alcohol and prepared for injection. No activity was present in the extract, showing a complete destruction due to the action of formaldehyde. In this respect this hormone is similar to relaxin since formaldehyde also destroys that hormone.

**Action of Nitrous Acid.**—Nitrous acid acts as a deaminizing agent on primary and secondary amines yielding alcohols and nitrosamines. If the active molecule of the hormone contains a primary or secondary amino group which is functional, nitrous acid would destroy the group and render the hormone inactive. The action of nitrous acid on the active preparation was therefore tried.

Ten cc. containing 50 rat units was acidified with glacial acetic acid (0.8 cc.) and treated with 2 cc. of 10% sodium nitrite solution. The solution was warmed to 35° for three hours, with occasional shaking. At the end of that period the solution was neutralized, concentrated, taken up in absolute alcohol and prepared for injection. Only about ten rat units was recovered from the fifty showing a marked decrease in activity.

**Action of Benzoyl Chloride.**—The presence of the primary or secondary amino group as well as OH groups might also be indicated by the action of benzoyl chloride. Experiments which demonstrate the effect of this reagent were carried out as follows.

Twenty cc. containing 100 rat units was dissolved in water and made alkaline ($P_H$ 9) by addition of sodium carbonate. Two cc. of benzoyl chloride was added and the mixture shaken in a tube for fifteen or twenty minutes. An appreciable amount of heat was liberated accompanied by evolution of carbon dioxide. The mixture was acidified and the benzoic acid removed by shaking with ether. The remaining aqueous solution was tested for activity but none was present.

Attempts to restore the activity by acid hydrolysis were made. In several instances small amounts of the activity seem to have been regenerated while in others the results were negative. However, the instances of apparent success would lead one to believe that success along this line might be accomplished by carefully regulating the conditions under which the hydrolysis is carried out. At the present time, however, the results must be considered as being negative.

**Action of Pepsin and Trypsin.**—Many of the hormones, such as insulin, relaxin, active principles of the posterior lobe of the hypophysis and the hormones of the anterior lobe of the hypophysis are destroyed by the action of proteolytic enzymes, indicating that they are probably of a type similar to peptides or polypeptides. The action of these enzymes on the mucifying hormone was investigated to determine if it can also be assigned to this general class.

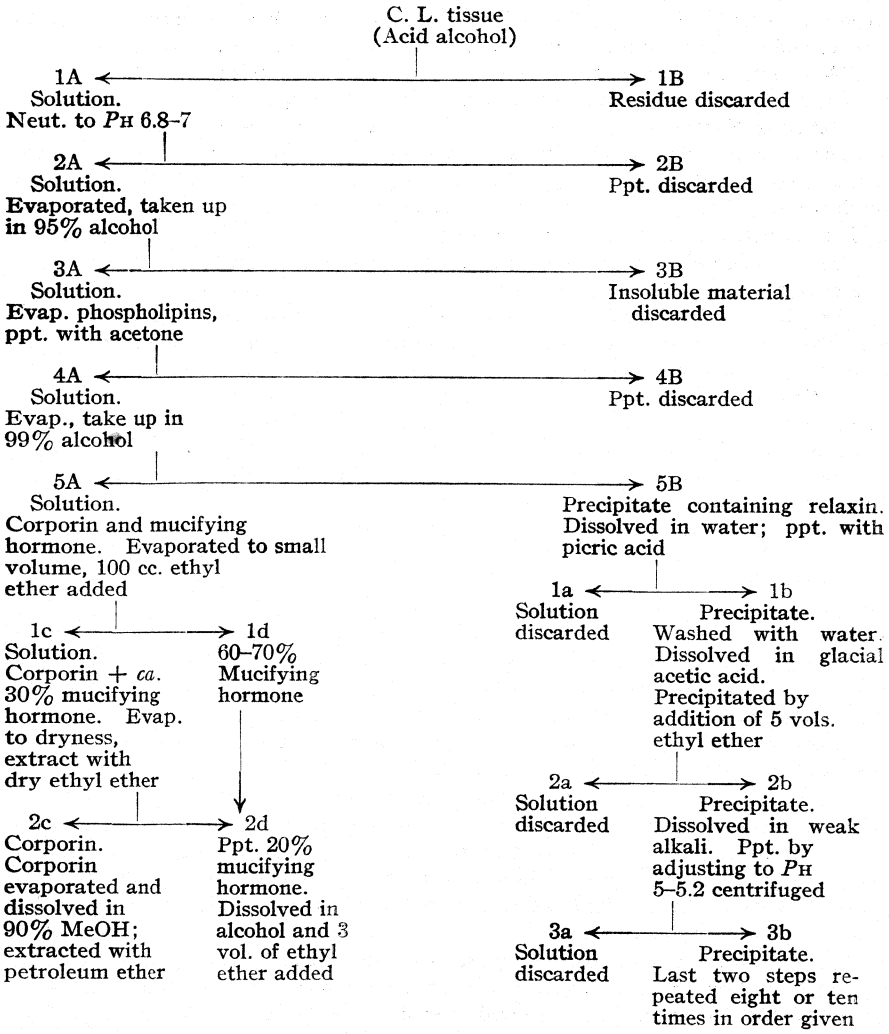
Twenty rat units was dissolved in an aqueous medium at a $P_H$ of 2.5 and subjected to peptic digestion for forty-eight hours. The solution was then concentrated almost to dryness, extracted with 99% alcohol and filtered. The filtrate was evaporated to dry-

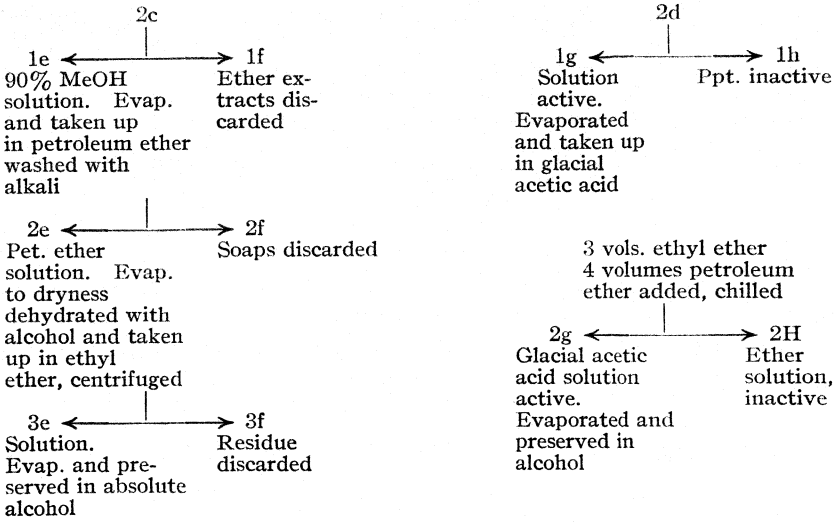
ness and the solute prepared for injection in saline solution. No decrease in activity could be detected since the twenty rat units was still present.

An equal amount of the mucifying hormone was dissolved in aqueous solution at a *P*H of 7.4 and subjected to tryptic digestion for forty-eight hours. At the end of that time the hormone was prepared for injection exactly as in the preceding experiment. As before the preparation retained its activity in full.

**Purification and Chemical Characteristics of Corporin.**—The alcoholic solution containing the corporin is evaporated to dryness and taken up in 50 cc. of methyl alcohol. The methyl alcohol solution may be packed in ice and the cholesterol partially chilled out by permitting it to stand for twenty-four to forty-eight hours, after which the crystallized cholesterol is centrifuged off, washed, reprecipitated and discarded.

SCHEMATIC DIAGRAM OF SEPARATION OF CORPUS LUTEUM HORMONES






To the methyl alcohol solution is added 5 cc. of water and the resulting 90% methyl alcohol is extracted three times with an equal volume of petroleum ether. The petroleum ether extracts are united and thoroughly washed with 90% methyl alcohol. The methyl alcohol solutions are then united. By this process none of the activity is lost to the petroleum ether and the methyl alcohol solution is free from all but traces of cholesterol and is active in 20-mg. doses. This step in purification may also be applied before the preliminary freezing out process.

The methyl alcohol solution is evaporated and taken up in petroleum ether. The petroleum ether solution is freed from any remaining fatty acids by the usual procedure of washing with dilute alkali until washings remain alkaline. The solution is freed from excess alkali by washing with acid and water. The soaps are washed with petroleum ether and discarded.

The resulting product is active in 15 to 20 mg. doses representing 25 to 50 g. of tissue. It is best preserved in absolute alcohol in a dark cool place. It must not be exposed to air for any length of time. For injection the material is dissolved in mazola oil so that it may be conveniently handled. It is not advisable, however, to keep it in this medium for more than four or five days.

The hormone is very unstable to alkalies since at a $P_H$ of 9.5–10 the activity decreases very rapidly. On the other hand it is very stable to heat and acids (under non-oxidizing conditions). This is amply demonstrated by the fact that the corpus luteum tissue may be refluxed with two volumes of acidified alcohol for three hours and the resulting extract instead of showing a decrease in activity shows an increase, undoubtedly due to more complete extraction since the acid completely disintegrates the tissue.

Extraction of the tissue by means of hot acid alcohol affords a quick and convenient method to obtain a very active extract for physiological purposes. As stated before, the relaxin is completely destroyed in this procedure. It is carried out as follows.

To one kilogram of the tissue in a 5-liter round-bottomed flask is added two liters of acidified alcohol. This is refluxed for two hours on a sand-bath after which the extract is removed from the residual tissue. The residue is washed with a liter of 95% alcohol and discarded. The extracts are neutralized, filtered, evaporated to dryness *in vacuo*, taken up in 95% alcohol, discarding any insoluble material. More inactive

material may be eliminated by again evaporating to dryness and extracting with 99% alcohol. The alcoholic solution is evaporated to dryness and extracted thoroughly with 200-cc. portions of acetone until the last portions of acetone are practically colorless. The acetone solution is evaporated and extracted with ether removing any insoluble material. The ether is evaporated and the solute is fractionated between 90% methyl alcohol and petroleum ether as before. The preparation thus obtained is active in twenty-five gram equivalents of the fresh tissue, varying somewhat depending on the activity of different lots of corpus luteum tissue.

## Discussion

In our preliminary report of the separation of relaxin from the active substance responsible for the other physiological reactions we stated that the preparation was water soluble. This was true but this preparation was far more active with respect to the mucifying factor than with respect to corporin. At that time we were using the mucifying reaction as our routine test in the laboratory and verifying our results with the pseudopregnancy reaction. The water-soluble preparation gave both reactions but as we later found much of the corporin was lost. Corporin may be prepared in aqueous medium but it is more soluble in organic solvents. The mucifying hormone, however, is readily soluble in water.

Corner and Allen[7,11] have prepared a neutral alcohol extract of corpus luteum tissue which contains a hormone which they call progestin. This is apparently the same hormone which we call corporin since it is the same in its physiological action and also similar chemically. Their crude preparation would also contain the mucifying hormone which is, however, eliminated in the process of purification by means of ethyl and petroleum ether. Relaxin is not extracted from the tissue by means of neutral alcohol. The method used by these workers is, however, efficient for the extraction of corporin but is rather time-consuming.

With regard to the chemical natures of these three hormones not much can be said conclusively at the present time. Relaxin as far as it has been characterized is quite similar to peptides or polypeptides. The mucifying hormone is not of this type since neither pepsin nor trypsin has any effect on the substance. However, formaldehyde which presumably acts on the amino group completely destroys the active molecules as do other agents which would act on this grouping. Corporin on the other hand is a fat-soluble substance and as such is different in nature from the other two corpus luteum hormones. It is more similar to the follicular hormone of the ovary, its main difference being its instability to alkalies.

## Summary

1. The corpora lutea of the sow secretes three active principles which have been extracted from the tissue and separated from one another.

2. The purification of the mucifying hormone and corporin is given.

[11] W. M. Allen, *Am. J. Phys.*, **92**, 174 (1930).

3. A few chemical characteristics of these two hormones are also given.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE QUEEN'S COLLEGE, OXFORD]

# THE CONDENSATION OF BUTYL CHLORAL HYDRATE WITH ARYL HYDRAZINES

BY FREDERICK DANIEL CHATTAWAY AND HARRY IRVING

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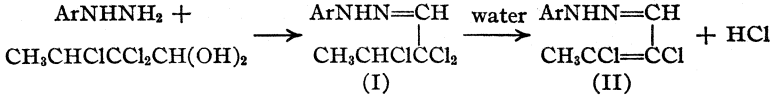
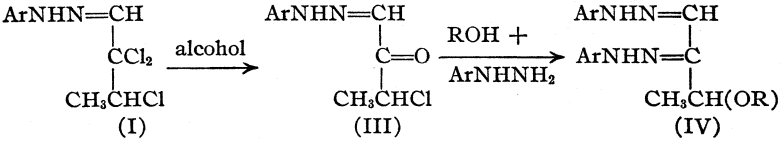
When butyl chloral hydrate is condensed with any aryl hydrazine, the hydrazone (I) first formed very readily undergoes a further reaction, the nature of which depends upon the solvent in which the change occurs.

In aqueous solution the initial hydrazone (I) loses hydrogen chloride and yields an *α,β-dichlorocrotonaldehyde-arylhydrazone* (II).[1]

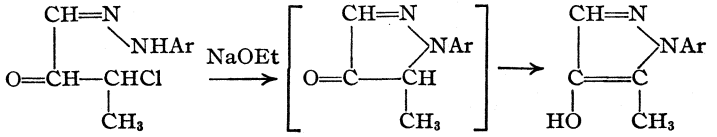



When, however, the condensation takes place in alcohol, the two α-chlorine atoms of the initial hydrazone (I) are replaced by an atom of oxygen and a *β-chloro-α-ketobutaldehyde-arylhydrazone* (III) is formed.[1]

These ketonic hydrazones (III) are very interesting substances for, when heated with a substituted arylhydrazine and any alcohol, many of them yield sparingly soluble *osazones* (IV) in which not only is the α-ketonic oxygen atom replaced by a hydrazine residue but also the remaining β-chlorine atom of the aldehyde chain is replaced by an alkoxy group.[1]




Again, when heated with an alcoholic solution of sodium ethoxide, these ketonic hydrazones (III) lose a molecule of hydrogen chloride, and ring closure takes place with the formation of the corresponding *4-hydroxy-1-aryl-5-methylpyrazoles* (V).[2] This reaction affords a general means of synthesis for these hitherto unknown 4-hydroxypyrazoles which are isomeric with the well-known 3- and 5-pyrazolones prepared from acetoacetic ester.

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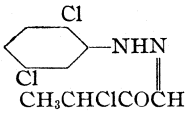
[1] Chattaway and Irving, *J. Chem. Soc.*, 87 (1930).

[2] Chattaway and Irving, *ibid.*, 786 (1931).

These reactions between butyl chloral hydrate and different arylhydrazines proceed with varying degrees of ease. With phenylhydrazine itself, and the three tolylhydrazines, the reaction, unless carefully controlled, may become very violent, when tarry products are formed from which nothing crystalline or definite can be isolated.[3] The introduction of halogens into the nucleus greatly moderates the violence of the initial reactions,[3] which proceed very smoothly when a 2,4-dihalogen substituted arylhydrazine is employed.[1]

It was of interest, therefore, to investigate the effect upon the character of the reaction and the nature of the products of the presence of two halogen atoms in other positions, and of the presence of three halogen atoms in the 2,4,6-positions of the phenylhydrazine residue.

It has been found that in alcoholic solution 2,5-dichloro-, 3,5-dichloro- and 4,5-dibromophenylhydrazine hydrochlorides condense quietly and normally with butyl chloral hydrate and yield the corresponding *β-chloro-α-ketobutaldehyde-arylhydrazones*.



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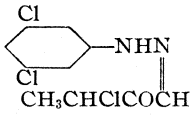

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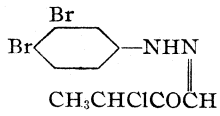

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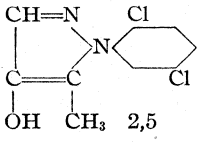
**β-Chloro-α-ketobutaldehyde-2,5-dichlorophenylhydrazone** condenses with 2,5-dichlorophenylhydrazine hydrochloride when heated in methyl or ethyl alcoholic solution and *α-keto-β-methoxy or ethoxy-butaldehyde-2,5-dichlorophenylosazone* (Formula as IV) is formed. When butyl chloral hydrate and 2,5-dichlorophenylhydrazine condense in methyl alcohol, the ketonic hydrazone and the methoxy-osazone are formed together and must be separated by fractional crystallization.

When treated with an alcoholic solution of sodium ethoxide these ketonic hydrazones yield the corresponding *4-hydroxy- 1-(2′,5′-dichloro-, or 3′,5′-dichloro-, or 4′,5′-dibromophenyl)-5-methylpyrazoles*



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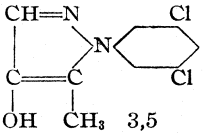

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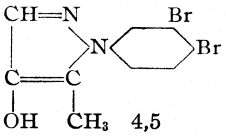

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which closely resemble in properties the previously described members of the series.[2]

Since the introduction of two halogen atoms into the nucleus in any position so greatly lessens the violence of the reaction which takes place between butyl chloral hydrate and unsubstituted, or methyl substituted,

[3] Chattaway and Irving, *J. Chem. Soc.*, 751 (1931).

phenylhydrazine, it might be anticipated that the introduction of a third halogen atom would further modify the reaction and this is found to be the case.

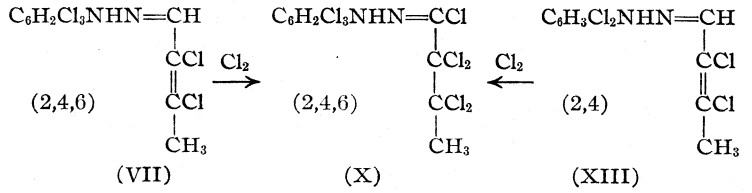
When butyl chloral hydrate and 2,4,6-trichlorophenylhydrazine hydrochloride interact in water, the unstable butyl chloral 2,4,6-trichlorophenylhydrazone (VI) first formed loses hydrogen chloride with the formation of *α,β-dichlorocrotonaldehyde-2,4,6-trichlorophenylhydrazone* (VII) alone.

When, however, the interaction takes place in alcohol, this decomposition of the initial hydrazone (VI) proceeds only to a slight extent and only a small quantity of the unsaturated hydrazone (VII) separates. In the remainder of the butyl chloral 2,4,6-trichlorophenylhydrazone (VI) the two α-chlorine atoms are hydrolyzed and replaced by an atom of oxygen with the formation of the pale yellow *β-chloro-α-ketobutaldehyde-2,4,6-trichlorophenylhydrazone* (VIII) which forms the bulk of the reaction product and remains dissolved in the mother liquors, whence it can only be separated and obtained free from the unsaturated hydrazone (VII) with the greatest difficulty.

When the unstable hydrazone (VI) formed by the interaction of butyl chloral hydrate and 2,4,6-trichlorophenylhydrazine hydrochloride in water is rapidly isolated by chloroform extraction, dried and warmed with acetic anhydride, acetylation occurs together with the hydrolysis of the two α-chlorine atoms and *N-acetyl-β-chloro-α-ketobutaldehyde-2,4,6-trichlorophenylhydrazone* (XI) is formed. This N-acetylhydrazone is also produced by the action of acetic anhydride upon β-chloro-α-ketobutaldehyde-2,4,6-trichlorophenylhydrazone (VIII) itself.

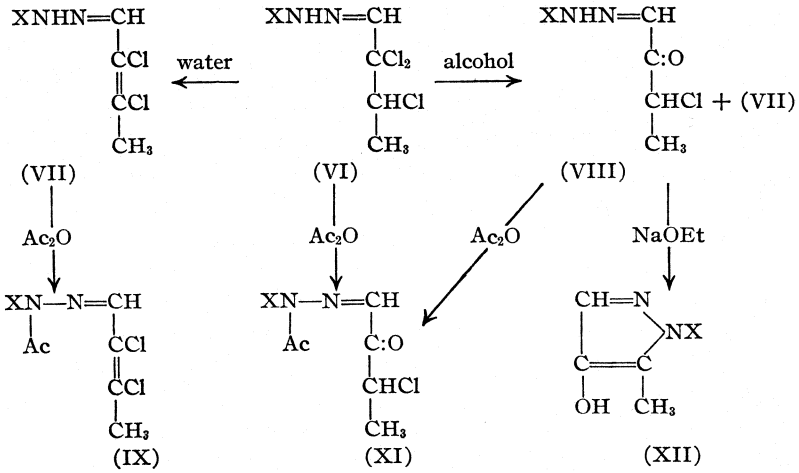
When β - chloro - α - ketobutaldehyde - 2,4,6 - trichlorophenylhydrazone (VIII) is warmed with an alcoholic solution of sodium ethoxide, loss of hydrogen chloride and ring closure take place with the formation of *4-hydroxy-1-(2′,4′,6′-trichlorophenyl)-5-methylpyrazole* (XII) which forms a *sodium salt*, a well characterized colorless *hydrochloride*, and a *4-benzoate*.

α,β-Dichlorocrotonaldehyde-2,4,6-trichlorophenylhydrazone (VII) yields a colorless *monoacetyl* derivative (IX) and when strongly reduced forms 2,4,6-trichloroaniline. On chlorination two atoms of chlorine are added at the double bond while a third substitutes the methine hydrogen atom yielding *ω,α,α,β,β - pentachlorobutaldehyde - 2,4,6 - trichlorophenylhydrazone* (X) identical with the product of chlorination of α,β-dichlorocrotonaldehyde-2,4-dichlorophenylhydrazone (XIII).[1]



A completely parallel series of reactions takes place when butyl chloral hydrate and 2,4,6-tribromophenylhydrazine hydrochloride interact in water, or in alcohol.

Thus, where X = 2,4,6-trichloro-, or tribromophenyl-




## Experimental Part

**The Action of 2,5-Dichlorophenylhydrazine Hydrochloride upon Butyl Chloral Hydrate in Ethyl Alcohol: Formation of β-Chloro-α-ketobutaldehyde-2,5-dichlorophenylhydrazone (VI).**—Ten grams of 2,4-dichlorophenylhydrazine hydrochloride (1 mol), 9 g. of butyl chloral hydrate (1 mol), and 75 cc. of ethyl alcohol were gently warmed together. As the reactants dissolved a bright red color developed and, when the boiling point of the alcohol was reached, a vigorous reaction set in, hydrogen chloride was freely evolved, and the alcohol continued to boil for some time without further heating. The bright red color gradually disappeared and the solution became pale yellow.

Half the alcohol was then distilled off and the concentrated solution left to cool, when *β-chloro-α-ketobutaldehyde-2,5-dichlorophenylhydrazone* separated as a mass of yellow crystals. It was collected, washed with a little cold ligroin and recrystallized from boiling alcohol, in which it was moderately soluble, and from which it separated in very slender flattened prisms of a pale lemon color, m. p. 142–143°.

*Anal.* Calcd. for $C_{10}H_9ON_2Cl_3$: Cl, 38.0. Found: Cl, 37.75.

The condensation of butyl chloral hydrate with 3,5-dichloro-, and with 4,5-dibromophenylhydrazine hydrochloride in ethyl alcohol proceeded similarly and yielded the following compounds.

**β-Chloro-α-ketobutaldehyde-3,5-dichlorophenylhydrazone** separated as compact prisms of a dull golden color, from a boiling 50% mixture of alcohol and pyridine, m. p. 118.5–120° (decomp.). It is very sparingly soluble in boiling alcohol.

*Anal.* Calcd. for $C_{10}H_9ON_2Cl_3$: Cl, 38.0. Found: Cl, 37.75.

**β-Chloro-α-ketobutaldehyde-4,5-dibromophenylhydrazone** separates from boiling 75% alcohol + 25% pyridine mixture in fine golden yellow prisms, m. p. 195–196° (decomp.). It is very sparingly soluble in boiling alcohol.

*Anal.* Calcd. for $C_{10}H_9ON_2ClBr_2$: Br, 43.4; Cl, 9.6. Found: Br, 43.6; Cl, 9.7.

**The Interaction of 2,5-Dichlorophenylhydrazine Hydrochloride with β-Chloro-α-ketobutaldehyde-2,5-dichlorophenylhydrazone in Methyl Alcohol: Formation of α-Keto-β-methoxybutaldehyde-2,5-dichlorophenylosazone.** (Formula as IV.)—Two grams of the hydrazone (1 mol) and 1.5 g. of 2,5-dichlorophenylhydrazine hydrochloride (1 mol) in 20 cc. of methyl alcohol were boiled for about five minutes and then cooled. The *osazone* (2 g.) which separated even at the boiling point of the alcohol (in which it is very sparingly soluble) was crystallized from boiling pyridine, in which it is readily soluble, and from which it separates in fine bright yellow compact prisms, m. p. 220° (decomp.).

*Anal.* Calcd. for $C_{17}H_{16}ON_4Cl_4$: Cl, 32.65. Found: Cl, 32.9.

**The corresponding ethoxy-osazone,** similarly prepared in ethyl alcoholic solution, crystallized from boiling alcohol–pyridine mixtures in fine bright yellow, highly refractive prisms with domed ends, m. p. 190° (with slight decomp.).

*Anal.* Calcd. for $C_{18}H_{18}ON_4Cl_4$: Cl, 31.65. Found: Cl, 31.6.

**The Interaction of Butyl Chloral Hydrate and 2,5-Dichlorophenylhydrazine Hydrochloride in Methyl Alcohol.**—When a powdered mixture of 10 g. of 2,5-dichlorophenylhydrazine hydrochloride (1 mol) and 9 g. of butyl chloral hydrate (1 mol) suspended in 25 cc. of methyl alcohol was treated in the way described for the reaction in ethyl alcohol (page 266), the same phenomena were observed as in that case; when cold, however, the reaction mixture had almost solidified to a pulp of crystals. These were separated and extracted with 50 cc. of boiling ethyl alcohol, a quantity (A) remaining undissolved. The solution, on cooling, deposited yellow needle-like crystals which after repeated crystallization from alcohol melted at 142–143°, alone or mixed with β-chloro-α-ketobutaldehyde-2,5-dichlorophenylhydrazone.

*Anal.* Calcd.: Cl, 38.0. Found: Cl, 37.95.

The material (A), after being extracted twice more with 50 cc. of boiling ethyl alcohol, left a yellow crystalline residue sparingly soluble in most of the common organic solvents; this separated from boiling pyridine, in which it was moderately easily soluble, in bright yellow, compact prisms, m. p. 220° (decomp.), identical with the methoxy-osazone described above.

*Anal.* Calcd.: Cl, 32.7. Found: Cl, 32.95.

**4-Hydroxy 1-(2′,5′-dichlorophenyl)-5-methylpyrazole** (V). (Ar = 2,5-Dichlorophenyl.)—Five grams of β-chloro-α-ketobutaldehyde-2,5-dichlorophenylhydrazone (1 mol) was added to a solution of 3 g. of sodium (2 mols + excess) in 100 cc. of ethyl alcohol. The deep orange solution produced was kept at room temperature for two hours, during which time sodium chloride separated, and was then very slowly heated to the boiling point of the alcohol and poured into 1000 cc. of boiling water. The rather turbid brown solution obtained was boiled with animal charcoal, filtered hot, concentrated to 250 cc., cooled and neutralized with hydrochloric acid; *4-hydroxy-1-(2′,5′-dichlorophenyl)-5-methylpyrazole* then separated as a sand-colored precipitate. This was dissolved in 100 cc. of hot 10% caustic potash solution, boiled with animal charcoal, and reprecipitated from the cooled filtrate by neutralization with hydrochloric acid. After repetition of this process it was crystallized from boiling acetone–light petroleum, from which it separated as colorless leaflets, m. p. 162–163°.

*Anal.* Calcd. for $C_{10}H_8ON_2Cl_2$: Cl, 29.2. Found: Cl, 29.1.

**1-(2′,5′-Dichlorophenyl)-5-methylpyrazolyl-4-benzoate** separated as a white solid when 1.3 g. of benzoyl chloride (1 mol + excess) was added to a vigorously shaken solution of 0.5 g. of the 4-hydroxypyrazole in 10 cc. of 10% aqueous potassium hydroxide. It is easily soluble in boiling alcohol from which it separates in colorless flattened prisms, m. p. 133–134°.

*Anal.* Calcd. for $C_{17}H_{12}O_2N_2Cl_2$: Cl, 20.4. Found: Cl, 20.7.

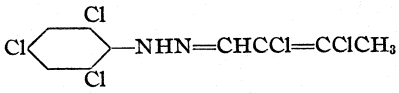
The action of sodium ethoxide upon alcoholic solutions of β-chloro-α-ketobutaldehyde-3,5-dichloro- (and 3,4-dibromo-)-phenylhydrazone yielded the corresponding 4-hydroxypyrazoles which were isolated and purified as described above (page 267).

**4-Hydroxy-1-(3′,5′-dichlorophenyl)-5-methylpyrazole** crystallizes from boiling chloroform, in which it is moderately soluble, in colorless prisms, m. p. 180–181°.

*Anal.* Calcd. for $C_{10}H_8ON_2Cl_2$: Cl, 29.2. Found: Cl, 29.0.

**4-Hydroxy-1-(3′,4′-dibromophenyl)-5-methylpyrazole** separates from acetone–light petroleum, in colorless slender prisms, m. p. 132–133°.

*Anal.* Calcd. for $C_{10}H_8ON_2Br_2$: Br, 48.2. Found: Br, 47.8.



**The Interaction of 2,4,6-Trichlorophenylhydrazine Hydrochloride with Butyl Chloral Hydrate in Water: Formation of α,β-Dichlorocrotonaldehyde-2,4,6-trichlorophenylhydrazone (VII).**—A solution of 18 g. of 2,4,6-trichlorophenylhydrazine hydrochloride (1 mol) in 800 cc. of water at 60° was added to a solution of 14 g. of butyl chloral hydrate (1 mol) in 600 cc. of water also at 60°. The mixture immediately became turbid, owing to the separation of yellow oily droplets, which turned first pink and then red, finally coalescing to form a viscous crimson mass. When cold, the supernatant liquid was decanted and the red viscous material was extracted with chloroform, in which it was readily soluble. The chloroform solution, after drying over calcium chloride, was kept at the ordinary temperature in an open dish for six days until the evolution of hydrogen chloride, which had been continuous from the first, had apparently ceased.

The chloroform had then evaporated, leaving a brown semicrystalline mass. The crystals were separated, washed free from viscous material with light petroleum, and recrystallized repeatedly from boiling alcohol (animal charcoal).

**α,β-Dichlorocrotonaldehyde-2,4,6-trichlorophenylhydrazone** crystallizes from boiling alcohol or acetic acid, in which it is only moderately soluble, in slender colorless prisms with a faint steel-blue reflex, m. p. 156–157°.

*Anal.* Calcd. for $C_{10}H_7N_2Cl_5$: C, 36.1; H, 2.1; N, 8.4; Cl, 53.3. Found: C, 36.4; H, 2.1; N, 8.4; Cl, 53.3.

**Reduction of α,β-Dichlorocrotonaldehyde-2,4,6-trichlorophenylhydrazone.**—Three grams of the hydrazone was dissolved in 20 cc. of glacial acetic acid and boiled with excess of zinc dust and 10 cc. of concentrated hydrochloric acid (one hour). *2,4,6-Trichloroaniline* which separated from the clear reaction mixture on dilution with water crystallized from dilute aqueous acetic acid, in slender prisms, m. p. 77°.

*Anal.* Calcd.: Cl, 54.2. Found: Cl, 54.0.

**The acetyl** derivative melted at 203°, alone or mixed with an authentic specimen.

$$\text{(2,4,6) } C_6H_2Cl_3NHN{=}CHCCl{=}CClCH_3 \xrightarrow{Cl_2} \text{(2,4,6) } C_6H_2Cl_3NHN{=}CClCCl_2CCl_2CH_3.$$

**Action of Chlorine upon α,β-Dichlorocrotonaldehyde-2,4,6-trichlorophenylhydrazone.**—A rapid stream of chlorine was passed into a suspension of 3 g. of the hydrazone in 10 cc. of glacial acetic acid. The temperature rose somewhat, hydrogen chloride was freely evolved, and a bright red color developed which gradually faded to a very faint yellow. When no further change appeared to be taking place (five minutes), the solution was set aside for twenty-four hours, during which time *α,α,β,β,ω-pentachlorobutaldehyde-2,4,6-trichlorophenylhydrazone* separated. This crystallized from boiling

acetic acid, in slender colorless prisms (phototropic), m. p. 84–85°, identical with the authentic specimen prepared by the chlorination of *α,β*-dichlorocrotonaldehyde-2,4-dichlorophenylhydrazone.[4]

When boiled with acetic anhydride containing a drop of concentrated sulfuric acid for several minutes, the octachlorohydrazone yielded *α,α,β,β,ω-pentachlorobutaldehyde-N-acetyl-2,4,6-trichlorophenylhydrazone*, m. p. 108–109° (acetic acid), alone or mixed with an authentic specimen.

**The Action of Acetic Anhydride upon *α,β*-Dichlorocrotonaldehyde-2,4,6-trichlorophenylhydrazone.**—This hydrazone is unchanged by boiling acetic anhydride. When, however, it is boiled with acetic anhydride containing a drop of concentrated sulfuric acid, acetylation proceeds smoothly and on cautious addition of water *α,β-dichlorocrotonaldehyde-N-acetyl-2,4,6-trichlorophenylhydrazone* separates as a colorless solid. It separates from boiling alcohol, in which it is readily soluble, in fine colorless compact rhombic prisms, m. p. 91–92° (decomp.).

*Anal.* Calcd. for $C_{12}H_9ON_2Cl_5$: C, 38.5; H, 2.5; N, 7.5; Cl, 47.3. Found: C, 39.0; H, 2.5; N, 7.4; Cl, 47.1.

**The Interaction of Butyl Chloral Hydrate with 2,4,6-Trichlorophenylhydrazine Hydrochloride in Ethyl Alcohol.**—Eighteen grams of 2,4,6-trichlorophenylhydrazine hydrochloride (1 mol) and 14 g. of butyl chloral hydrate (1 mol) were warmed with 150 cc. of ethyl alcohol. As the reactants dissolved a bright red color developed but on heating to 50–60° for a short time the color faded to orange and finally a clear pale yellow solution was obtained. After standing for twenty-four hours at the ordinary temperature 0.75 g. of *α,β-dichlorocrotonaldehyde-2,4,6-trichlorophenylhydrazone* (VII) (m. p. 156–157° from alcohol) separated, identical with the compound previously obtained (page 268) when the reaction was carried out in water.

The mother liquors, concentrated to 50 cc. by distillation of the alcohol under reduced pressure (50 mm.), were poured into water (1000 cc.) and extracted with benzene. The benzene extracts, dried over sodium sulfate, were allowed to evaporate spontaneously when a viscid mass of *β-chloro-α-ketobutaldehyde-2,4,6-trichlorophenylhydrazone* (VIII) remained which solidified when repeatedly triturated with ligroin and seeded with a crystal obtained from a previous preparation. The crude solid (13–14 g.) so obtained was collected, washed with light petroleum to remove adhering viscous material, and recrystallized to constant chlorine analysis from a boiling mixture of benzene and light petroleum (animal charcoal).

**β-Chloro-α-ketobutaldehyde-2,4,6-trichlorophenylhydrazone** is very soluble in cold alcohol, chloroform, acetone and acetic acid, moderately soluble in cold benzene, and very sparingly soluble in 40–60° petroleum ether, or water. It separates from a boiling mixture of benzene and light petroleum in compact yellow monoclinic prisms with domed ends, m. p. 107–109°.

*Anal.* Calcd. for $C_{10}H_8ON_2Cl_4$: C, 38.2; H, 2.55; N, 8.9; Cl, 45.2. Found: C, 38.1; H, 2.5; N, 9.15; Cl, 45.6.

When vigorously reduced with tin and boiling hydrochloric acid this hydrazone yielded 2,4,6-trichloroaniline, which was identified by its acetyl derivative, m. p. 203°.

When boiled for several minutes with acetic anhydride containing a drop of concentrated sulfuric acid, this hydrazone yielded *β-chloro-α-ketobutaldehyde-N-acetyl-2,4,6-trichlorophenylhydrazone* (XI) which separated from boiling alcohol, in which it is readily soluble, in colorless rhombic plates, m. p. 136–137°.

*Anal.* Calcd. for $C_{12}H_{10}O_2N_2Cl_4$: C, 40.6; H, 2.8; N, 7.9; Cl, 39.8. Found: C, 40.9; H, 3.0; N, 8.5; Cl, 39.8.

[4] Chattaway and Irving, *J. Chem. Soc.*, 91 (1930).

The same compound was obtained by the action of acetic anhydride upon butyl chloral 2,4,6-trichlorophenylhydrazone itself. Ten grams of 2,4,6-trichlorophenylhydrazine hydrochloride (1 mol) in 600 cc. of water at 60° and 6 g. of butyl chloral hydrate (1 mol) in 500 cc. of water also at 60° were allowed to interact as described above (page 268). After five minutes the whole was cooled rapidly and the *butyl chloral 2,4,6-trichlorophenylhydrazone* which had separated as a viscous mass was extracted with chloroform and dried over calcium chloride. The chloroform was then removed rapidly by a current of hot air and 20 cc. of acetic anhydride was added to the residue, when a brisk exothermic reaction ensued, the red color faded to a pale yellow, and a crystalline mass of *β-chloro-α-ketobutaldehyde-N-acetyl-2,4,6-trichlorophenylhydrazone* separated, identical with the above.

*Anal.* Calcd.: Cl, 39.8. Found: Cl, 39.7.

**4-Hydroxy-1-(2′,4′,6′-trichlorophenyl)-5-methylpyrazole (XII)** was prepared by warming β-chloro-α-ketobutaldehyde-2,4,6-trichlorophenylhydrazone (5 g.) with a solution of 3 g. of sodium (excess) in 50 cc. of ethyl alcohol, and was isolated and purified in the same way as the 4-hydroxypyrazoles described above (page 267).

**4-Hydroxy-1-(2′,4′,6′-trichlorophenyl)-5-methylpyrazole** crystallizes from a boiling mixture of chloroform and petroleum ether (b. p. 60–80°) in well-developed colorless prisms, m. p. 152–153°.

*Anal.* Calcd. for $C_{10}H_7ON_2Cl_3$: Cl, 38.3. Found: Cl, 38.3.

It dissolves in boiling concentrated hydrochloric acid, in which it is somewhat sparingly soluble, and on cooling the *hydrochloride*, $C_{10}H_7ON_2Cl_3 \cdot HCl$, separates in fine colorless prisms with domed ends, m. p. 175° (decomp.). When dissolved in water, it is hydrolyzed quantitatively to the parent 4-hydroxypyrazole, m. p. 152°.

**The sodium salt** of 4-hydroxy-1-(2′,4′,6′-trichlorophenyl)-5-methylpyrazole $C_{10}H_6N_2Cl_3(ONa)$ separates rapidly as a felt of colorless prisms on cooling a solution of the 4-hydroxypyrazole in warm 20% caustic soda solution.

**1-(2′,4′,6′-Trichlorophenyl)-5-methylpyrazolyl-4-benzoate,** prepared by the Schotten–Baumann reaction, crystallizes from boiling alcohol in colorless flattened prisms with domed ends, m. p. 113°.

*Anal.* Calcd. for $C_{17}H_{11}O_2N_2Cl_3$: Cl, 27.9. Found: Cl, 28.0.

The interaction of butyl chloral hydrate with 2,4,6-tribromophenylhydrazine hydrochloride in water, or in alcohol, yields an entirely analogous series of compounds.

**α,β-Dichlorocrotonaldehyde-2,4,6-tribromophenylhydrazone** crystallizes from boiling alcohol, in which it is rather sparingly soluble, in faintly colored needles, m. p. 157°.

*Anal.* Calcd. for $C_{10}H_7N_2Br_3Cl_2$: C, 25.75; H, 1.5; N, 6.0; Cl + Br, 66.75. Found: C, 26.1; H, 1.7; N, 6.3; Cl + Br, 66.9.

**α,β-Dichlorocrotonaldehyde-N-acetyl-2,4,6-tribromophenylhydrazone** separates from boiling alcohol, or acetic acid, in which it is readily soluble, in compact colorless rhombic plates, m. p. 113–114° (decomp.).

*Anal.* Calcd. for $C_{12}H_9ON_2Cl_2Br_3$: Cl, 14.0; Br, 47.2. Found: Cl, 14.0; Br, 47.4.

**β-Chloro-α-ketobutaldehyde-2,4,6-tribromophenylhydrazone** separates from a mixture of benzene and light petroleum in rosets of pale yellow prisms, m. p. 122–123° (decomp.).

*Anal.* Calcd. for $C_{10}H_8ON_2ClBr_3$: Cl, 7.9; Br, 53.6. Found: Cl, 7.9; Br, 53.45.

**β-Chloro-α-ketobutaldehyde-N-acetyl-2,4,6-tribromophenylhydrazone** crystallizes from boiling alcohol (sparingly soluble) in colorless rhombic plates, m. p. 171–172°.

*Anal.* Calcd. for $C_{12}H_{10}O_2N_2ClBr_3$: C, 29.4; H, 2.1; N, 5.7; Cl, 7.25; Br, 49.0. Found: C, 29.4; H, 2.1; N, 5.7; Cl, 7.3; Br, 49.25.

**4-Hydroxy-1-(2′,4′,6′-tribromophenyl)-5-methylpyrazole** separates from a mixture of boiling chloroform and light petroleum (b. p. 60–80°) in short colorless prisms, m. p. 177.5–178°.

*Anal.* Calcd. for $C_{10}H_7ON_2Br_3$: Br, 58.4. Found: Br, 58.5.

**1-(2′,4′,6′-Tribromophenyl)-5-methylpyrazolyl-4-benzoate** separates from boiling alcohol in clusters of colorless rhombic prisms, m. p. 128–130°.

*Anal.* Calcd. for $C_{17}H_{11}O_2N_2Br_3$: Br, 46.6. Found: Br, 46.5.

## Summary

1. The influence of halogens in the nucleus upon the character of the reaction and the nature of the products obtained when arylhydrazines condense with butyl chloral hydrate in various solvents, is described.

2. 2,5-Dichloro-, 3,5-dichloro- and 4,5-dibromophenylhydrazines condensed in alcohol yield the corresponding β-chloro-α-ketobutaldehyde-arylhydrazones.

3. 2,4,6-Trichloro (or bromo-)-phenylhydrazine condensed in water yields α,β-dichlorocrotonaldehyde-2,4,6-trichloro(or bromo-)-phenylhydrazone, but, when condensed in alcohol, a mixture of this unsaturated hydrazone with β-chloro-α-ketobutaldehyde-2,4,6-trichloro (or bromo)-phenylhydrazone.

4. All the β-chloro-α-ketobutaldehyde-arylhydrazones yield the corresponding members of the new series of 4-hydroxy-1-aryl-5-methylpyrazoles when treated with an alcoholic solution of sodium ethoxide.

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[CONTRIBUTION FROM THE LABORATORIES OF GEORGE PINESS, M.D., LOS ANGELES]

# *dl*-BETA-PHENYLISOPROPYLAMINES

BY GORDON A. ALLES

RECEIVED AUGUST 10, 1931 PUBLISHED JANUARY 7, 1932

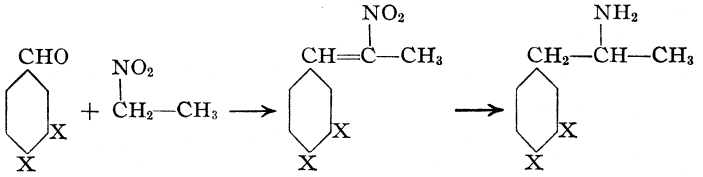
In a previous paper[1] it was demonstrated with *dl*-β-phenylisopropylamine that the introduction of a methyl group into the side chain of β-phenylethylamine furnishes a compound differing from the latter with regard to certain of its effects when administered as a drug compound. The *dl*-β-phenylisopropylamine exerts a pressor effect for a longer period of time and is quite effective after oral administration. Because of the very considerable importance of developing drug compounds of this general type that are active after oral administration, it seemed important to study some derivatives of *dl*-β-phenylisopropylamine having one or more hydroxyl groups introduced into the benzene ring.

The compounds of particular interest for this study, *dl*-β-4-hydroxyphenylisopropylamine and *dl*-β-3,4-dihydroxyphenylisopropylamine, have

[1] Piness, Miller and Alles, *J. Am. Med. Assn.*, **94**, 790 (1930).

been synthesized previously[2] but no satisfactory description of their physiological activities is available. Further, the methods used for synthesis were rather involved and it seemed desirable to develop a simpler synthesis of this type of compound for use in the present study. The syntheses of the parent *dl*-β-phenylisopropylamine and the desired hydroxy derivatives are reported in this paper; the physiological studies of the compounds prepared will be reported in another place.

The synthesis of β-phenylethylamines is often accomplished, especially for proof of structure, by condensing an aromatic aldehyde with nitromethane under suitable conditions and complete reduction of the ω-nitrostyrene so formed, to the hydrogenated amine derivative. It was found that a similar preparative process can be carried out with nitroethane in place of nitromethane, the resultant product being a *dl*-β-phenylisopropylamine.




The initial condensation step in the process was found to be most simply carried out by the method of Knoevenagel and Walther[3] when the X groups were H, $OCH_3$ or similarly substituted hydroxyl, but condensation does not occur by this method when one or both of the groups is an hydroxyl. The second step, the complete reduction, involves considerable difficulty but the described electrolytic reduction method gives fair yields of the desired amines while several attempts at catalytic hydrogenation or reduction with various metals or their amalgams were not at all successful. Since the initial condensation step of the above process does not occur when the X groups are hydroxyl, it was necessary to demethylate the corresponding methoxyl derivatives of phenylisopropylamine to obtain the desired hydroxyphenylisopropylamines. This was attempted following the procedure of Mannich and Jacobsohn,[2] using concentrated hydriodic acid, but no satisfactory product could be isolated from the demethylation of *dl*-β-4-methoxyphenylisopropylamine by this method. However, demethylation with concentrated hydrochloric acid under pressure did yield a good preparation of the desired *dl*-β-4-hydroxyphenylisopropylamine hydrochloride.

## Experimental Part

The details of preparation of the *dl*-β-phenylisopropylamine and its 4-methoxy and 3,4-dimethoxy derivatives differ only in the aldehyde used and the intermediate and final products isolated.

[2] Mannich and Jacobsohn, *Ber.*, **43**, 189 (1910).

[3] Knoevenagel and Walther, *ibid.*, **37**, 4502 (1904).

**Condensation of Aldehyde and Nitroethane.**—0.2 Mole of aldehyde, 0.2 mole of nitroethane and 0.02 mole of *n*-amylamine were mixed and set aside at room temperature in the dark. After a day water began to separate from the mixture; after several days the mixture became quite solid. After two weeks, the mixture was dissolved to a homogeneous solution by warming with 50 cc. of ethanol and then on cooling a fine crystal product was obtained. From benzaldehyde, 0.15 mole of phenylnitropropylene melting at 65–66° was obtained. The melting point of this compound has been reported as 64°.[3] From anisaldehyde, 0.15 mole of 4-methoxyphenylnitropropylene melting at 43–44° was obtained. The melting point of this compound has been reported as 48°.[3] From veratraldehyde, 0.31 mole of 3,4-dimethoxyphenylnitropropylene melting at 70–71° was obtained.

**Reduction of Phenylnitropropylenes.**—0.1 Mole of phenylnitropropylene dissolved in a catholyte of 100 cc. of ethanol, 50 cc. of acetic acid and 50 cc. of 12 *N* sulfuric acid was placed above a 40-sq. cm. mercury cathode in a porous cell surrounded by a 3 *N* sulfuric acid anolyte with a water-cooled lead anode. Four amperes was passed for twenty hours and the temperature in the catholyte was kept between 30 and 40°.

The resultant catholyte was partially evaporated, then made strongly alkaline and the separated basic layer taken up with benzene. The desired amine was then extracted from the benzene by just neutralizing with dilute hydrochloric acid and separating the aqueous layer. This was then evaporated and the product crystallized. From phenylnitropropylene, 0.02 mole of *dl*-β-phenylisopropylamine hydrochloride melting at 144–145° was obtained. The melting point of this compound has been reported as 145–147°.[4]

*Anal.* Subs., 0.1737: 20.22 cc. of 0.05 *N* $AgNO_3$. Calcd. for $C_9H_{14}NCl$: Cl, 20.67. Found: Cl, 20.64.

From 4-methoxyphenylnitropropylene, 0.02 mole of *dl*-β-4-methoxyphenylisopropylamine hydrochloride melting at 208–209° was obtained. The melting point of this compound has been reported as 210°.[2]

*Anal.*, Subs., 0.1000: 9.90 cc. of 0.05 *N* $AgNO_3$. Calcd. for $C_{10}H_{16}ONCl$: Cl, 17.59. Found: Cl, 17.56.

From 3,4-dimethoxyphenylnitropropylamine, 0.02 mole of *dl*-β-3,4-dimethoxyphenylisopropylamine hydrochloride melting at 151–152° was obtained. The melting point of this compound has been previously reported as 144°.[2]

*Anal.* Subs., 0.1400: 12.10 cc. of 0.05 *N* $AgNO_3$. Calcd. for $C_{11}H_{18}O_2NCl$: Cl, 15.31. Found: Cl, 15.32.

**Demethylation of *dl*-β-4-Methoxyphenylisopropylamine.**—Five grams of *dl*-β-4-methoxyphenylisopropylamine hydrochloride was placed in a pressure bottle with 20 cc. of concentrated hydrochloric acid and heated in an autoclave under 15 pounds per sq. in. steam pressure for six hours. The product was evaporated to dryness and then crystallized from ethanol and ether; 3.8 g. of crystals melting at 171–172° was obtained. These are readily soluble in water and alcohol. The water solution gives no coloration with a ferric chloride solution but gives positive phenol tests with Millon and Folin reagents.

*Anal.* Subs., 0.1500: 15.97 cc. of 0.05 *N* $AgNO_3$. Calcd. for $C_9H_{14}ONCl$: Cl, 18.90. Found: Cl, 18.88.

**Demethylation of *dl*-β-3,4-Dimethoxyphenylisopropylamine.**—Three grams of *dl*-β-3,4-dimethoxyphenylisopropylamine hydrochloride was boiled with 15 g. of hydriodic acid (sp. gr. 1.7) through which was passed a stream of carbon dioxide gas. After twenty minutes the major portion of the hydriodic acid was distilled off and the residue

[4] Hey, *J. Chem. Soc.*, 18 (1930).

shaken with an aqueous suspension of freshly precipitated silver chloride. After filtering off the insoluble silver salts, the filtrate was evaporated. With much difficulty a crystalline product was obtained, 1.5 g. of gray-white crystals melting at 192°. The melting point of this compound has been previously reported as 190–192°.[2] The product is readily soluble in water and alcohol. The water solution gives a green coloration with a ferric chloride solution and a blue coloration with Folin phosphotungstic reagent after making alkaline.

*Anal.* Subs., 0.010: 0.68 mg. of N as $NH_3$ by micro-Kjeldahl analysis. Calcd. for $C_9H_{14}O_2NCl$: N, 6.87. Found: N, 6.8.

## Summary

1. A new synthetic method for preparing *dl*-β-phenylisopropylamine and certain of its derivatives has been developed.

2. 4-Hydroxy- and 3,4-dihydroxyphenylisopropylamines have been prepared by this method for physiological studies.

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[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

# SOLUBILITY RELATIONSHIPS AMONG OPTICALLY ISOMERIC SALTS.

# I. THE MALATES OF ALPHA-PARA-XENYLETHYLAMINE[1]

BY A. W. INGERSOLL AND E. G. WHITE

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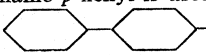
In previous papers a method has been described by which it is possible,[2] in certain instances, to obtain both active forms of an externally compensated base or acid in an optically pure condition. For example, in the resolution of a base (*dl*B), as much as possible of one active form, for instance, *l*B, is obtained in the usual way by Pasteur's third method. The residual, partially active base (*dl*B + *d*B) is then recovered from the mother liquors, combined with any suitable inactive (externally compensated) acid (*dl*A) and the salts fractionally crystallized. In this step either of two mixtures of salts may be obtained, depending on whether the inactive acid is resolved by the active base present in excess (Equation 1) or forms a stable, partially racemic salt with it (Equation 2).

$$(dl\text{B} + d\text{B}) + dl\text{A} \longrightarrow dl\text{B}dl\text{A} + d\text{B}d\text{A} + d\text{B}l\text{A} \quad (1)$$

$$(dl\text{B} + d\text{B}) + dl\text{A} \longrightarrow dl\text{B}dl\text{A} + d\text{B}dl\text{A} \quad (2)$$

According to the usual results of fractional crystallization it may be expected that when any of the salts containing only the active base (here *d*B) is the least soluble, it can be purified and a complete resolution of the base results. On the other hand, should the totally racemic salt be the least

[1] The radical name *p*-xenyl is used in this paper as a brief designation of the *p*-diphenylyl radical,  .

[2] Ingersoll, THIS JOURNAL, **47**, 1168 (1925); **50**, 2264 (1928).

soluble, the salt containing the desired active base usually cannot be purified and the completion of the resolution fails.

In the earlier papers the possible scope and limitations of the method were briefly discussed, but it was pointed out that more experimental data and a closer analysis of the underlying theory were desirable. The success of the method obviously depends upon a favorable order of solubility of the salts concerned. The solubility order, however, is known only for the few instances previously reported and thus far no basis for predicting it in individual instances is apparent. It was decided, therefore, to continue the study experimentally by examining as many instances as possible of the use of the method with a view to determine its convenience, and to provide materials for the study of solubilities. Also, on the theoretical side, it was decided to study more fully the fundamental question of solubility relationships among optically isomeric salts.

In this paper there is presented an analysis of the possible systems and solubility relationships of the salts that may be involved when the method for complete resolution is applied in its usual form as outlined above, and in a modified form. Also a general consideration of solubility relationships is briefly introduced. In the experimental part an additional instance of the use of the method is described. Other instances in which the method is being used or in which solubility relationships are being studied will be described, it is hoped, in later papers.

**Systems Resulting from the Usual Procedure.**—In the absence of some natural regularity in the order of solubility, the salts resulting from the combination of an externally compensated acid with a partially active base may be arranged, so far as their solubilities are concerned, into eight possible cases, representing five experimentally different situations, as follows

$$\begin{cases} (1) & (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < dl\text{B}dl\text{A} \\ (2) & (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < dl\text{B}dl\text{A} \end{cases}$$

$$\begin{cases} (3) & (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < dl\text{B}dl\text{A} < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) \\ (4) & (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < dl\text{B}dl\text{A} < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) \end{cases}$$

$$\begin{cases} (5) & dl\text{B}dl\text{A} < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) \\ (6) & dl\text{B}dl\text{A} < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) \end{cases}$$

$$(7) \quad (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A}$$

$$(8) \quad dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A})$$

When an externally compensated base is combined with a partially active acid, exactly the same cases are possible except that in (7) and (8) the partially racemic salts are the *dl*B*d*A or *dl*B*l*A types.

If it may be assumed that the order of separation in fractional crystallization is determined mainly by solubility, then in Cases 1,2,3,4 and 7 a successful completion of the resolution is possible. In Cases 5,6 and 8, while the proportion of the salts containing active components may be increased by the removal of a portion of the inactive salt in the head fractions, the complete purification of the desired active salts can succeed only in excep-

tional instances. If it may be expected that Cases 1–6, which depend on mutual resolvability of the acid and base, will be encountered equally often, then the method should be successful in two-thirds of these instances. Should Cases 7 and 8 occur more often than Cases 1–6, as seems probable from the prevalence of stable partially racemic salts, there is then an even chance that the solubility order will be favorable. An important object of the work now in progress is to determine how often each case occurs.

**Systems Resulting from a Modified Procedure.**—In the foregoing discussion there has been considered only that procedure for possible complete resolution which employs a completely inactive acid (or base) in the second step. It may, however, occasionally be convenient to combine a partially active base with an equivalent amount of a partially active acid, either for the purpose of completing a resolution or of obtaining some one of the resulting salts pure. For illustration, equivalent amounts of the partially active mixtures (*dl*B + *d*B) and (*dl*A + *d*A) may be combined, with the results shown in the following equations.

$$(dl\text{B} + d\text{B}) + (dl\text{A} + d\text{A}) \longrightarrow dl\text{B}dl\text{A} + (d\text{B}dl\text{A} \text{ or } dl\text{B}d\text{A}) + d\text{B}d\text{A} \quad (3)$$

$$(dl\text{B} + d\text{B}) + (dl\text{A} + dA) \longrightarrow dl\text{B}dl\text{A} + (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) + d\text{B}d\text{A} \quad (4)$$

The nature of the first or second alternative salt in the second term on the right side of the equations depends upon whether the inactive acid or the inactive base, respectively, is present in greater proportion, and upon whether the partially racemic salt corresponding to this is stable (Equation 3) or unstable (Equation 4). In the event that the inactive acid and base are present in the same proportion, the second term disappears (Equation 5).

$$(dl\text{B} + d\text{B}) + (dl\text{A} + d\text{A}) \longrightarrow dl\text{B}dl\text{A} + d\text{B}d\text{A} \quad (5)$$

When the possible orders of solubility are considered for the combination of any partially active acid and partially active base, it is clear that the salt mixtures resulting from Equations 4 and 5 constitute cases identical with or simpler than Cases 1–6 described above, and involve no new solubility relationships. The mixtures resulting from Equation 3, however, involve twelve new solubility relationships, grouped into six experimentally similar pairs. When the inactive acid is in greater proportion, the cases are as follows

$$\begin{cases} (9) & (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A} \\ (10) & (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A} \end{cases}$$

$$\begin{cases} (11) & (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) \\ (12) & (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) \end{cases}$$

$$\begin{cases} (13) & (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < dl\text{B}dl\text{A} \\ (14) & (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) < dl\text{B}dl\text{A} \end{cases}$$

$$\begin{cases} (15) & (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A} < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) \\ (16) & (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < dl\text{B}dl\text{A} < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) \end{cases}$$

$$\begin{cases} (17) & dl\text{B}dl\text{A} < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) \\ (18) & dl\text{B}dl\text{A} < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) \end{cases}$$

$$\begin{cases} (19) & dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < (d\text{B}d\text{A} \text{ or } l\text{B}l\text{A}) \\ (20) & dl\text{B}dl\text{A} < (d\text{B}dl\text{A} \text{ or } l\text{B}dl\text{A}) < (d\text{B}l\text{A} \text{ or } l\text{B}d\text{A}) \end{cases}$$

When the inactive base is in greater proportion twelve parallel cases are possible in which the partially racemic salts are the *dl*B*d*A or *dl*B*l*A types.

When fractional crystallization is applied it appears that Cases 9–12 favor the purification of salts containing both active acid and active base and may result in complete resolution. Cases 13–16 yield pure partially racemic salts containing one active component, though this may not be the one desired for complete resolution and may be present in small amount. Instances that fall in these cases in the modified procedure would, however, fall in the favorable Case 7 in the usual procedure. Cases 17–20 are unfavorable for complete resolution, but permit the recovery of the pure inactive components and the concentration of the active components from materials otherwise of little value. The modified procedure is being used in this Laboratory mainly as a supplement to the usual procedure in instances in which the solubility order is known to be favorable, but it may be seen that instances falling in the favorable cases (11) and (12) in the modified procedure would fall in the unfavorable Case 8 in the usual procedure.

It should be noted that either procedure is subject to the usual limitation of fractional crystallization, so that theoretically possible separations may be too tedious in practice. On the other hand, some or all of the salts may separate with solvent of crystallization and the degree of solvation or even the order of solubility may differ in different solvents or at different temperatures. These possibilities do not in any way invalidate the foregoing analysis, but instead are as likely as not to convert an unfavorable into a favorable case. A further element of flexibility in the method lies in the fact that the inactive or partially active acid or base used in the second step may be selected from those available after preliminary trials have indicated a favorable result. In Cases 1–4 and 9–12 the inactive or partially active resolving agent is itself resolved.

In previous papers there were described two instances that are now recognized as illustrating Case 4, and one illustrating Case 7. These resulted in complete resolution. The present paper contains a description of an instance in which an attempt to complete the resolution by the usual procedure failed (Case 8) but in which the resolution was ultimately completed by the modified procedure (Case 12). Thus inactive α-*p*-xenylethylamine ($C_6H_5C_6H_4CH(NH_2)CH_3$) was first partially resolved with *l*-malic acid. The less soluble *d*B*l*A salt and the component *d*-base were obtained pure. The solubility of this salt was 1.95 g. per 100 g. of water at 25°. The base recovered from the mother liquors (*dl*B + *l*B) was then combined with *dl*-malic acid and the salts were crystallized. The *dl*B*dl*A salt separated first and was purified. Its solubility was 2.42 g. per 100 g. of water at 25°. Though a part of the inactive base was in this way re-

moved from the mixture, the *l*B*d*l*A* salt remaining in the foot fractions could not be purified. The modified procedure was then employed. Another sample of the partially active base (as hydrochloride) was combined with a sample of partially active malic acid (as acid ammonium salt) which contained a considerable excess of the *d*-form. From the solubilities recorded above it was predicted that the *l*B*d*A salt should be the first to crystallize. This was verified by the experiment and this salt and the component *l*-base were obtained pure.

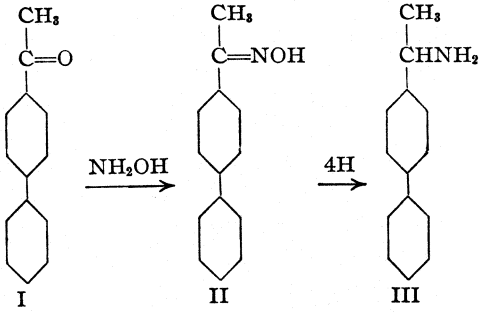
**Extension of the Solubility Problem.**—When the question of solubility relationships is considered from a general viewpoint it will be recalled that the active and inactive forms of a base and an acid may form a maximum of five differently soluble types (including nine varieties) of salts, as follows

(*d*B*d*A or *l*B*l*A); (*d*B*l*A or *l*B*d*A); *dl*B*dl*A; (*d*B*dl*A or *l*B*dl*A); (*dl*B*d*A or *dl*B*l*A)

The first three types are always capable of existence; the partially racemic types only when they happen to be stable in solution. Since a mixture of any two or more of the five types, if put into solution in any proportions, could not constitute or change into a system more complicated than those described in the preceding sections, the relative solubilities of as many as four or five of these types will never be concerned in any process based upon fractional crystallization. Nevertheless, it would appear that a knowledge of the solubility relationships of all of the stable types should have considerable theoretical interest.

In the absence of any extensive experimental data, it does not seem appropriate to set forth the obviously large number of possible solubility orders, but it is intended to record the solubilities for particular instances whenever the necessary salts can be prepared. In a previous paper the order for the camphor-10-sulfonates of isodiphenylhydroxyethylamine was reported as (*d*B*d*A or *l*B*l*A) < (*d*B*dl*A or *l*B*dl*A) < (*d*B*l*A or *l*B*d*A) < *dl*B*dl*A. The *dl*B*d*A or *dl*B*l*A salt is unstable. In the present work the malates of $\alpha$-*p*-xenylethylamine are found to be in the order (*d*B*l*A or *l*B*d*A) < *dl*B*dl*A < *d*B*dl*A or *l*B*dl*A < (*d*B*d*A or *l*B*l*A). The *dl*B*d*A or *dl*B*l*A salt is unstable.

The $\alpha$-*p*-xenylethylamine (III) used in these experiments was obtained by the reduction of the oxime (II) of *p*-phenylacetophenone (I).




I II III

This new base is one of a group of analogs of α-phenylethylamine now being studied. It was prepared in the hope that it might possess the advantages of α-phenylethylamine as a resolving agent, but would be a water-insoluble solid more convenient to handle than the parent base. It proved to be a sparingly soluble liquid which solidified only in an ice-bath. It is best purified and handled in the form of its sparingly soluble hydrochloride. Its use as a resolving agent is being further studied.

## Experimental Part

**p-Phenylacetophenone** was prepared by a method similar to that of Drake and Bronitsky.[3] Material melting at 117–119° was used to prepare the oxime. A specimen regenerated from the oxime melted at 120° (corr.).

**p-Phenylacetophenone Oxime.**—The ketone (98 g., 0.5 mole) was dissolved in 500 cc. of 95% ethanol and hydroxylamine hydrochloride (45 g., 0.65 mole) and 100 cc. of 30% sodium hydroxide was added. The mixture was refluxed for five hours on a water-bath. A part of the oxime, together with sodium chloride, separated from the hot solution; most of the remainder separated on cooling. The solid was filtered by suction, washed with warm water to remove salt and when dry was crystallized from about ten parts of 95% ethanol. It separates as pale yellow irregular plates, m. p. 186° (corr.). The yield was 80–82%.

*Anal.* Calcd. for $C_{14}H_{13}ON$: N, 6.64. Found: N, 6.73.

**α-p-Xenylethylamine.**—An attempt to reduce the oxime with sodium and absolute alcohol failed because of the precipitation of the insoluble sodium salt. The reduction was readily accomplished with sodium amalgam. Twenty grams of the crude oxime was dissolved in 350 cc. of 95% ethanol on a water-bath and 700 g. of 3% sodium amalgam was added during an hour, with sufficient glacial acetic acid to keep the mixture always faintly acid. When the reaction had ceased most of the alcohol was distilled with steam and the amine was liberated with excess alkali and extracted with benzene. After drying and removing the solvent, the crude amine remained as a brown oil which set to a solid mass in a freezing mixture but liquefied on coming to room temperature. It partially decomposed on attempted distillation at 10 mm. pressure, could not be crystallized from any of the common solvents and gradually formed a carbonate in contact with air. It is most conveniently purified and kept in the form of its sparingly soluble hydrochloride, from which it is regenerated as a colorless water-insoluble liquid. The yield calculated from the hydrochloride was 80–87% in several preparations.

**Hydrochloride.**—The crude amine was dissolved in an excess of hot 5% hydrochloric acid and the solution filtered. The hydrochloride was recrystallized from water with decolorizing carbon. For analysis a sample was recrystallized from 95% ethanol and again from water. The salt forms glistening white needles, m. p. 221° (corr.). A sample placed on the lip induces slight numbness and irritation.

*Anal.* Calcd. for $C_{14}H_{16}NCl$: Cl, 15.18. Found: Cl, 15.27.

**Benzoyl Derivative.**—A sample of the pure hydrochloride was shaken with dilute sodium hydroxide and benzoyl chloride. The amide crystallized from 95% ethanol in small prisms, m. p. 179° (corr.).

*Anal.* Calcd. for $C_{21}H_{19}ON$: N, 4.65. Found: N, 4.55.

**Partial Resolution of the *dl*-Base.**—In preliminary experiments the base was combined with various active acids and the salts examined to determine the most suitable

[3] Drake and Bronitsky, THIS JOURNAL, **52**, 3715 (1930).

resolving agent. The salt formed with *d*-bromocamphor-$\pi$-sulfonic acid separated from water as an oil and could not be satisfactorily crystallized from any of the usual solvents. The acid *d*-tartrate crystallized readily from water or from 95% ethanol. The hydrochloride of the base from the head fractions had a small dextro rotation but the separation was too slow to be useful. The *d*-camphor-10-sulfonate separated from water or dilute ethanol partly as hair-like needles, partly as an oil which later solidified. Systematic fractionation gave results similar to those with the tartrate. The base was readily resolved through the acid *l*-malate.

The base (calcd. 42.2 g.) was recovered from 50 g. of the pure hydrochloride and combined with 28.5 g. of *l*-malic acid in 600 cc. of hot water. The solution deposited a dense crust of faintly colored crystals and smaller crops of similar crystals were obtained by concentrating the mother liquor. When this was reduced to about 100 cc. it slowly set to a semi-solid mass on cooling, but the more soluble *l*B*l*A salt could not be purified. By systematic crystallization of the less soluble fractions there was finally obtained 30.3 g. of pale yellow crystals of the nearly pure *d*B*l*A salt. Recrystallization from 95% ethanol, in which the salt is less soluble than in water, removed the color and a trace of insoluble solid. The pure salt weighed 28 g. (calcd. 35.4 g.).

***d*-$\alpha$-*p*-Xenylethylamine-*l*-malate** crystallizes from ethanol or water in glistening plates, m. p. 183° (corr.), and is anhydrous. Its faint dextro rotation could not be measured accurately. An aqueous solution (11.133 g.) saturated at 25° contained 0.2125 g. of salt, from which the solubility is 1.95 g. per 100 g. of water.

***d*-$\alpha$-*p*-Xenylethylamine.**—A sample of the pure *l*-malate was dissolved in hot water and decomposed with ammonium hydroxide. The base closely resembles the inactive variety described above. It was purified as the hydrochloride in nearly quantitative yield, calculated from the acid malate. A sample of the base was regenerated from the hydrochloride, washed several times by decantation with warm water and dried to constant weight in the absence of carbon dioxide.

*Rotation.* Subs. 2.2302 g. made up to 25 cc. in 95% ethanol gave $\alpha_D^{25}$ +2.21° in a 1-dm. tube, hence $[\alpha]_D^{25}$ +24.8°.

**Hydrochloride.**—This was prepared as described for the inactive form, which it closely resembles. It melts at 230° (corr.) and is slightly less soluble in water than the inactive form.

*Anal.* Calcd. for $C_{14}H_{16}NCl$: Cl, 15.18. Found: Cl, 15.06.

*Rotation.* Subs. 1.0105 g. made up to 50 cc. in water gave $\alpha_D^{25}$ +0.52° in a 2-dm. tube, hence $[\alpha]_D^{25}$ +12.8; $M_D$ +30°.

In another experiment the resolution was repeated with minor variations in the details of the fractionation, but with similar results. The hydrochloride of the base finally obtained had $[\alpha]_D^{25}$ +12.7°.

**Attempted Completion of the Resolution with *dl*-Malic Acid.**—The mother liquors from the partial resolutions described above were combined and the base was liberated and converted to hydrochloride in the usual way. The specific rotation of the latter was −9.4°, from which it was calculated that about 76% excess of the *l*-form was present. A sample of this salt (23.4 g.) was converted to the base (calcd. 19.7 g.) and this was combined with 13.5 g. of *dl*-malic acid in 225 cc. of hot water. The solution on cooling deposited a crust of small crystals. The decanted solution on further standing deposited a loose mass of small spherules. The material obtained by concentrating the mother liquor was similar to the second crop. When the first fraction was crystallized twice from water and once from 95% ethanol there was obtained 6.6 g. of small anhydrous prisms, m. p. 170° (corr.). The salt was optically inactive. The hydrochloride of the base obtained from a sample of the salt melted at 221° and was optically inactive. The salt is therefore the *dl*B*dl*A type. A specimen prepared from the pure inactive hydro-

chloride and an equivalent amount of *dl*-ammonium acid malate had identical properties. An aqueous solution (9.666 g.) saturated at 25° contained 0.2331 g. of salt, from which the solubility is 2.42 g. per 100 g. of water.

The more soluble fractions of the malate upon further crystallization gave a small additional amount of the inactive salt but the main portion, presumably the *l*B*dl*A salt, could not be purified. The hydrochloride of the base obtained from the combined foot fractions had $[\alpha]_D^{25}$ −11.2°. For comparison the enantiomorphous *d*B*dl*A salt was prepared from the pure *d*-base and *dl*-malic acid. It crystallizes from water or ethanol in nodules or as a microcrystalline mass, m. p. 173°, and is anhydrous. An aqueous solution (10.1805 g.) saturated at 25° contained 0.2820 g. of salt, from which the solubility is 2.84 g. per 100 g. of water.

**Completion of the Resolution with Partially Active Malic Acid.**—A sample of the base hydrochloride (6.6 g.) containing about 68% excess of the *l*-form was dissolved in 100 cc. of water and there was added 4.3 g. of ammonium acid malate containing about 80% excess of the *d*-form. The latter had been previously obtained by a partial resolution of *dl*-malic acid with cinchonine.[4] A powdery solid separated on standing. When this was crystallized four times from water and once from 95% ethanol, it weighed 3.4 g. The salt was identified as the *l*B*d*A type. It melted at 182–183° (corr.) and closely resembled the *d*B*l*A salt described above. The material contained in the mother liquors was not further examined.

**1-α-*p*-Xenylethylamine Hydrochloride.**—The pure *l*B*d*A salt was decomposed with ammonium hydroxide solution and the base converted to hydrochloride. This melted at 230° (corr.) in exact agreement with the corresponding *d*-form.

*Rotation.* Subs. 1.2343 g. made up to 50 cc. in water gave $[\alpha]_D^{25}$ −0.60° in a 2-dm. tube, hence $[\alpha]_D^{25}$ −12.2°.

The authors are indebted to Dr. R. L. Jenkins of the Swann Corporation for a generous supply of pure diphenyl.

## Summary

1. An analysis of the solubility relationships among the salts resulting from the combination of inactive and partially active acids and bases is presented, with particular reference to the problem of complete optical resolution.

2. The preparation of α-*p*-xenylethylamine and the appropriate intermediates and derivatives and the complete resolution of the base through its salts with active and inactive malic acids are described.

NASHVILLE, TENNESSEE

[4] Dakin, *J. Biol. Chem.*, **59**, 7 (1924).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# THE REACTION OF ORGANIC HALIDES WITH PIPERIDINE. II. CERTAIN ALPHA-BROMO-BETA-KETONIC ESTERS

BY B. W. HOWK AND S. M. MCELVAIN

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As a preliminary to some work which was contemplated in this Laboratory it was necessary to determine the course of the reaction of secondary amines, such as piperidine, with the three esters, ethyl α-bromobenzoylacetate, ethyl α-bromo-α-benzoylpropionate and ethyl α-bromo-α-phenylbenzoylacetate.

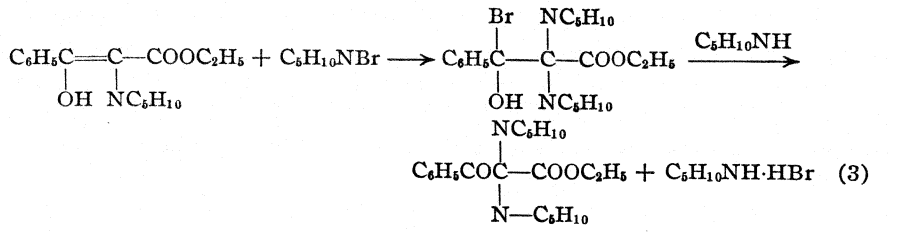
A study of the reaction of piperidine with a variety of alkyl bromides has been reported.[1] In this work it was found that the primary bromides were very much more reactive than the secondary or tertiary bromides and that the primary and secondary bromides, with the exception of cyclohexyl bromide, reacted with the piperidine to form tertiary amines, while cyclohexyl bromide and the tertiary bromides gave no tertiary amines but lost hydrogen bromide under the influence of the piperidine. The bromo esters mentioned above would seem to offer an interesting extension of this type of study, for the reason that they are secondary and tertiary bromides the reactivity of which would be considerably enhanced by the associated groups of each molecule.

No attempt was made to carry out the reaction of these bromo esters with piperidine under similar conditions. Rather those conditions which produced a quite complete reaction as indicated by the yield of piperidine hydrobromide were found and used in each case. It was found that the optimum ratio of reactants was one mole of the bromo ester to three moles of piperidine.

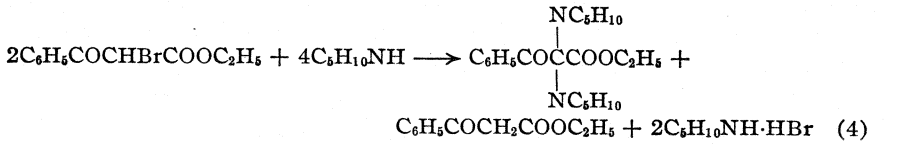
Ethyl α-bromobenzoylacetate reacted rapidly with piperidine in dry ether and after a few hours 90% of the theoretical quantity of piperidine hydrobromide was precipitated. From the ethereal solution ethylbenzoyl acetate and a compound of the molecular formula, $C_{21}H_{30}O_3N_2$, which proved to be ethyl α,α-dipiperidinobenzoylacetate were isolated. The amounts of these two compounds which were obtained represented in the case of the former, 30% and in the case of the latter, 39% of the original bromo ester. Their formation may be illustrated by the following reactions

$$C_6H_5COCHBrCOOC_2H_5 + C_5H_{10}NH \longrightarrow C_5H_{10}NBr + C_6H_5COCH_2COOC_2H_5 \quad (1)$$

$$C_6H_5COCHBrCOOC_2H_5 + 2C_5H_{10}NH \longrightarrow C_5H_{10}NH\cdot HBr + C_6H_5COCHCOOC_2H_5 \quad (2)$$
$$\qquad\qquad\qquad

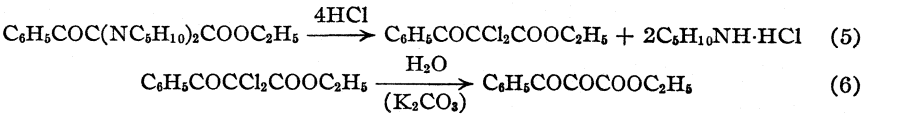


The sum of reactions 1, 2 and 3 gives the net reaction as



The bromination of piperidine by the bromo ester with the formation of ethyl benzoyl acetate and N-bromopiperidine (Reaction 1) is analogous to the behavior of diphenylbenzoylmethyl bromide as a brominating agent recently reported by Koelsch.[2] Reaction 2 is the normal reaction that would be expected between a secondary halide and piperidine.[1] Reaction 3 which involves the addition of N-bromopiperidine to the enol form of the monopiperidino compound seems probable from the work of Foldi,[3] who has shown that N-halogenated amines and amides add readily to the olefinic double bond. Such an addition product would be directly decomposed by the excess of piperidine present into the dipiperidino compound and piperidine hydrobromide.

The structure of the ethyl $\alpha,\alpha$-dipiperidinobenzoylacetate is shown by the following facts. As mentioned above, analyses and molecular weight determinations show it to have a molecular formula of $C_{21}H_{30}O_3N_2$. On alkaline hydrolysis it was converted into benzoic acid, ethyl alcohol and two moles of piperidine for each mole of the original compound. An ethereal solution of one mole of $C_{21}H_{30}O_3N_2$ when treated with dry hydrogen chloride yielded two moles of piperidine hydrochloride. From the resultant ethereal solution, after washing with potassium carbonate, ethyl benzoylglyoxalate, $C_6H_5COCOCOOC_2H_5$, was obtained. The formation of this latter compound may be explained by the following reactions:



Finally ethyl $\alpha,\alpha$-dipiperidinobenzoylacetate was prepared by the action of piperidine on ethyl $\alpha,\alpha$-dibromobenzoylacetate and was found to be

[2] (a) Koelsch, THIS JOURNAL, 53, 1147 (1931); (b) *cf.* also Goldschmidt and Nagel, *Ber.*, 63, 1212 (1930).

[3] Foldi, *ibid.*, 63, 2257 (1930).

identical with the compound obtained from the reaction of piperidine with ethyl $\alpha$-bromobenzoylacetate.

The reaction of ethyl $\alpha$-bromo-$\alpha$-benzoylpropionate and piperidine in ether gave, after about seven hours, a 75% yield of piperidine hydrobromide. A longer period of reaction in ether solution did not increase the yield of this salt, but if the ether was distilled off and the remaining reactants heated at the temperature of the steam-bath for one hour, an additional 23% yield of piperidine hydrobromide was obtained. When the reaction mixture was worked up ethyl $\alpha$-benzoylpropionate and a compound, melting at 132–133° and having the molecular formula $C_{22}H_{32}O_3N_2$ were isolated in yields that represented 35 and 28%, respectively, of the original bromo ester. The latter compound had a neutral equivalent of 187 and was ethyl $\alpha$-benzoyl-$\alpha,\beta$-dipiperidinopropionate. The reactions by which these products were formed may be illustrated thus

$$C_6H_5COC(CH_3)BrCOOC_2H_5 + C_5H_{10}NH \longrightarrow C_6H_5COCH(CH_3)COOC_2H_5 + C_5H_{10}NBr \quad (7)$$

$$C_6H_5COC(CH_3)BrCOOC_2H_5 + C_5H_{10}NH \longrightarrow C_6H_5COC(=CH_2)COOC_2H_5 + C_5H_{10}NH\cdot HBr \quad (8)$$

$$C_6H_5COC(=CH_2)-COOC_2H_5 + C_5H_{10}NBr \longrightarrow C_6H_5COC(CH_2Br)(NC_5H_{10})COOC_2H_5 \quad (9)$$

$$C_6H_5COC(CH_2Br)(NC_5H_{10})COOC_2H_5 + 2C_5H_{10}NH \longrightarrow C_6H_5COC(CH_2NC_5H_{10})(NC_5H_{10})COOC_2H_5 + C_5H_{10}NH\cdot HBr \quad (10)$$

The reactions 7, 8, 9 and 10 give as the net reaction,

$$2C_6H_5COC(CH_3)BrCOOC_2H_5 + 4C_5H_{10}NH \longrightarrow C_6H_5COCH(CH_3)COOC_2H_5 + C_6H_5COC(CH_2NC_5H_{10})(NC_5H_{10})COOC_2H_5 + 2C_5H_{10}NH\cdot HBr \quad (11)$$

In reaction 7 the ethyl $\alpha$-benzoylpropionate is formed as a result of the brominating action of the bromo ester. The loss of halogen acid from the ester (reaction 8) would be expected[1] from the fact that it is tertiary halide and the addition of N-bromopiperidine to the benzoylacrylic ester thus formed is analogous to reaction 3 and the reactions reported by Foldi.[3] The fact that the last portion of the halogen could not be obtained as piperidine hydrobromide until the temperature of reaction was raised to 100°, indicates that the bromo compound formed in reaction 9 is an unactivated primary bromide.[1]

Ethyl $\alpha$-phenyl-$\alpha$-bromobenzoyl acetate gave no precipitate of piperidine hydrobromide when refluxed in an ether solution of piperidine for seven hours. When, however, the ether was removed and the residue heated for two hours on a steam-bath a 95% yield of piperidine hydro-

bromide was obtained. When this salt was removed and the remainder of the reaction mixture worked up, a 10% yield of the ethyl α-phenylbenzoylacetate and a 60% yield of ethyl benzoate together with a small amount of ethyl phenylacetate were obtained. The residue from the distillation of these esters which had been extracted with both acid and alkali gave piperidine on hydrolysis. These results indicate that the bromo ester, by brominating the piperidine, is converted into the ethyl α-phenylbenzoylacetate, which reacts with piperidine under the conditions used to form an amide. The alcohol liberated in the latter reaction then splits the keto amide and keto ester. These reactions may be illustrated as

$$C_6H_5COCBr(C_6H_5)COOC_2H_5 + C_5H_{10}NH \longrightarrow C_6H_5COCH(C_6H_5)COOC_2H_5 + C_5H_{10}NBr \quad (12)$$

$$C_6H_5COCH(C_6H_5)COOC_2H_5 + C_5H_{10}NH \longrightarrow C_6H_5COCH(C_6H_5)CONC_5H_{10} + C_2H_5OH \quad (13)$$

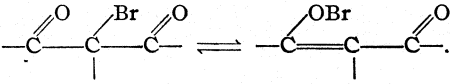
$$C_6H_5COCH(C_6H_5)COOC_2H_5 + C_2H_5OH \longrightarrow C_6H_5COOC_2H_5 + C_6H_5CH_2COOC_2H_5 \quad (14)$$

The piperidine hydrobromide which is obtained from the reaction quite probably results from a disproportionation of N-bromopiperidine. Lellmann[4] has shown that N-chloropiperidine in the presence of alkali loses hydrogen chloride to form tetrahydropyridine and piperidine hydrochloride and that on heating it disproportionates into N-chlorotetrahydropyridine and piperidine hydrochloride. It seems reasonable that N-bromopiperidine would follow a similar reaction course under the conditions used in the work now described. The following reaction, then, would explain the elimination of practically all of the bromine from the reactants as piperidine hydrobromide

$$C_5H_{10}NBr + C_5H_{10}NH \longrightarrow C_5H_9N + C_5H_{10}NH\cdot HBr \quad (15)$$

The action of piperidine on the three α-bromo-β-keto esters as described above is of some interest in connection with the previous work on the relation of structure to the course of the reaction of organic halides with piperidine. The replacement of the secondary halogen of ethyl α-bromobenzoylacetate to form a tertiary amine and of the tertiary halogen of ethyl α-bromo-α-benzoylpropionate to form the intermediate α-benzoylacrylic ester parallels the behavior of the simple secondary and tertiary bromides with piperidine.[1] The brominating action of each of the bromo esters is a separate and distinct competing reaction which has no counterpart in the case of the alkyl bromides. Ethyl α-phenyl-α-bromobenzoylacetate is a tertiary bromide which cannot lose hydrogen bromide. It is by far the least reactive of the three bromo esters studied and when it is forced into reaction with the secondary amine it shows only the brominating action. Professor C. S. Marvel of the University of Illinois has suggested to the authors that the brominating action of this type of bromo ester may be due to a hypobromite structure. If such be the case it would

[4] Lellmann, *Ber.*, **21**, 1924 (1888).

seem quite probable that these bromo esters exist in the following tautomeric forms,  .

## Experimental

**Materials Used.**—The sodium ethoxide was prepared and the various esters which were used were purified by the procedure given by McElvain.[5] Piperidine was prepared by the catalytic reduction of purified pyridine in the presence of nickel.[6] Ethyl benzoylacetate was prepared by the procedure of Claisen and Lowman.[7] Ethyl α-benzoylpropionate was prepared in a similar manner by the condensation of ethyl benzoate with the ethyl propionate. This compound has been prepared previously[8] by the methylation of ethyl benzoylacetate.

**Cyanodesoxybenzoin.**—This compound has been prepared by Walther and Schickler[9] by the direct condensation of ethyl benzoate with benzyl cyanide. They obtained a yield of only 10% of the theoretical. In the present work the following procedure, which gave a yield of 47% of cyanodesoxybenzoin, was used. A mixture of 80 g. (1 mol) of benzyl cyanide, 300 g. (3 mols) of ethyl benzoate and 46 g. of sodium ethoxide were placed in a flask equipped with an efficient mechanical stirrer and a condenser set for downward distillation. The mixture was stirred rapidly and gradually heated to 220° on an oil-bath. The alcohol distilled as formed and was collected. At the end of seven hours no more alcohol came over and the mixture was allowed to cool. A yield of 29 g. (48.5%) of alcohol was obtained. The red gelatinous mass in the flask was shaken with a mixture of ice water and ether until all the salt had dissolved. The ether layer was separated and the water layer again extracted with ether. After separation of the ether layer, the aqueous portion was acidified with dilute sulfuric acid. A mixture of benzoic acid and cyanodesoxybenzoin separated as an oil which later solidified. The solid mixture was filtered and recrystallized from 95% alcohol. The remaining benzoic acid was effectively removed by suspending the solid in a saturated solution of sodium bicarbonate and shaking vigorously. The undissolved cyanodesoxybenzoin was filtered and washed with water. After drying it weighed 71 g. (47.5%) and melted at 89–90°.

**Ethyl α-Phenylbenzoylacetate.**—This compound has been prepared by Walther and Schickler[9] and by Scheibler[10] by the alcoholysis of cyanodesoxybenzoin. Since neither of these investigators gave satisfactory experimental details or yield of product, the following method of preparation, which was used in the present work, is given. A solution of 55 g. of cyanodesoxybenzoin in 300 g. of absolute alcohol was cooled to 0° and saturated with dry hydrogen chloride. After standing overnight at room temperature the alcohol was removed by distillation under reduced pressure and the solid imino ester hydrochloride taken up in 100 cc. of alcohol to which 10 cc. of water had been added. The resulting mixture was refluxed for one hour, after which it was poured into 3 liters of ice water. The ethyl α-phenylbenzoylacetate separated out and was filtered. After recrystallization from 95% alcohol it melted at 89–90°. The yield was 41.8 g. (63%).

[5] McElvain, THIS JOURNAL, **51**, 3124 (1929).

[6] The authors are indebted to Messrs. K. A. Folkers and R. A. Connor for this preparation.

[7] Claisen and Lowman, *Ber.*, **20**, 651 (1887).

[8] Perkin and Calmen, *J. Chem. Soc.*, **49**, 156 (1886).

[9] Walther and Schickler, *J. prakt. Chem.*, [2] **55**, 308 (1897).

[10] Scheibler, *Ber.*, **63**, 1564 (1930).

**Bromination of the Keto Esters.**—Each of the keto esters mentioned above was brominated by the gradual addition of the theoretical quantity of bromine to the ester in boiling carbon tetrachloride solution. After the bromine had been absorbed the solvent was removed by distillation and the residue distilled under diminished pressure. The yields, physical constants and analyses of the bromo esters are summarized in the following table.

| Compound, ethyl | Yield, % | B. p. (1 mm.), °C. | $d_{20}^{20}$ | $n_D^{20}$ | Analyses, % Br Calcd. | Found |
|---|---|---|---|---|---|---|
| α-Bromo benzoylacetate | 90 | 135–137 | 1.4092 | 1.5470 | 29.49 | 29.40 |
| α-Dibromo benzoylacetate | 71 | 153–154 | 1.7127 | 1.5703 | 45.71 | 43.91[a] |
| α-Bromo benzoylpropionate | 79 | 148–150 | 1.3499 | 1.5340 | 28.07 | 28.27 |
| α-Bromophenylbenzoylacetate[b] | 85 | 189–190 | .... | .... | 23.07 | 24.02 |

[a] The analyses for this compound were low due to the fact that it was not possible to separate all of the monobromo ester from it by fractional distillation. [b] All analyses of this compound were high because of traces of hydrogen bromide which could not be removed. This bromo ester has not been described heretofore in the literature although the possibility of its formation has been mentioned by Scheibler.[10] It is quite unstable and appears to decompose in a few hours. It is a heavy, yellow, viscous oil with a slight lachrymatory effect.

**Reaction of the α-Bromo-β-keto Esters with Piperidine.**—In the case of ethyl α-bromobenzoylacetate a solution of 100 g. (1 mol) of the bromo ester in 100 cc. of ether was added slowly from a dropping funnel to a solution of 97 g. (3 mols) of piperidine in 300 cc. of ether contained in a 1-liter flask which was fitted with an efficient reflux condenser. The reaction was sufficiently exothermic to cause vigorous boiling of the ether at the beginning of the addition. An immediate precipitation of piperidine hydrobromide occurred. After stirring for seven hours the salt was filtered, dried and weighed. A yield of 57 g. of the hydrobromide, representing 90% of the bromine in the reaction mixture, was obtained. The ether was distilled from the filtrate and the last traces removed by a water pump. A pasty yellow mass, consisting of a crystalline substance and an oil, remained in the flask. To this residue 100 cc. of 95% alcohol was added whereupon the oil went into solution and the crystals remained undissolved. The latter were filtered off and recrystallized from light petroleum ether. A yield of 53.25 g. of pale yellow crystals which melted at 131–132° was obtained. The alcoholic filtrate was evaporated under reduced pressure and the residue again taken up in ether and the ethereal solution washed first with dilute sulfuric acid then with dilute potassium carbonate solution. The solution was dried with sodium sulfate, the ether evaporated and the residue distilled under reduced pressure. A yield of 22.1 g. of ethyl benzoylacetate boiling at 118–120° (1 mm.) was obtained.

The pale yellow crystals which were insoluble in alcohol were identified as ethyl α,α-dipiperidinobenzoylacetate. This compound was basic and dissolved readily in dilute hydrochloric acid but could not be recovered when the solution was made alkaline. Long boiling with 30% alkali and steam distillation gave 93% of *two* moles of piperidine for each mole of the solid compound. This piperidine was isolated as the benzene sulfonamide, m. p. 94°. Benzoic acid and ethyl alcohol were also obtained from this hydrolysis. On passing dry hydrogen chloride into an ethereal solution of 10 g. of the substance, 6.6 g. of piperidine hydrochloride was obtained. This amount of piperidine hydrochloride indicated that the two piperidine nuclei had been split out of the molecule and recovered in a 98% yield.

Nothing definite could be isolated from the ethereal solution directly after the treatment with hydrogen chloride except a small amount of a viscous lachrymatory oil, but

when the ethereal solution was washed with potassium carbonate solution, evaporation of the ether and distillation yielded 4.5 g. of a yellow-orange oil boiling at 128–130° (1 mm.). This oil was identified as ethyl benzoylglyoxalate. On hydrolysis with 15% hydrochloric acid, 0.840 g. of the oil gave 0.47 g. of benzoic acid and 0.1754 g. of carbon dioxide which represent 95 and 98% yields, respectively. The identification was completed by the preparation of the mono-oxime, which melted at 123°.[11]

Ethyl α,α-dipiperidinobenzoylacetate was prepared also from ethyl α,α-dibromobenzoylacetate in the following manner. A solution of 5 g. of the dibromo ester in 50 cc. of ether was treated with 6 g. of piperidine and the mixture refluxed for fifty hours. After this time the piperidine hydrobromide was filtered off and from the ethereal solution 1.6 g. of a compound was isolated which proved to be identical with the ethyl α,α-dipiperidinobenzoylacetate obtained above by the action of piperidine on the ethyl α-bromobenzoylacetate.

In the case of ethyl α-bromo-α-benzoylpropionate a solution of 43.5 g. (1 mol) of the bromo ester and 39 g. (3 mols) of piperidine in 500 cc. of ether was placed in a 1-liter flask fitted with a reflux condenser. Precipitation of piperidine hydrobromide began immediately. After stirring for seven hours the hydrobromide was filtered and weighed. About 75% of the theoretical amount was formed at that time. Continued stirring of the solution gave no further precipitation of piperidine hydrobromide, so the flask was transferred to a steam-bath and the ether removed by distillation. The residue was heated on the steam-bath for one hour and again taken up in ether. Another portion of piperidine hydrobromide precipitated and was filtered from the solution. The total yield of this salt was 25 g., which represented 98% of the bromine in the original solution. When the ether was distilled from the solution, a pasty yellow mass remained in the flask. The addition of 100 cc. of alcohol caused the oily portion of this residue to dissolve, leaving a crystalline substance suspended in the solution. These crystals were filtered off and recrystallized from 95% alcohol. A yield of 16 g. of pale yellow crystals which melted at 132–133° was obtained. Removal of the alcohol from the filtrate gave a heavy red oil which was taken up in ether and washed with dilute sulfuric acid and then with dilute potassium carbonate solution. On evaporation of the ether and distillation of the oily residue 11 g. of ethyl α-benzoylpropionate was obtained.

The yellow crystals were identified as ethyl α,β-dipiperidino-α-benzoylpropionate. On hydrolysis they gave benzoic acid and piperidine. The substance was basic and had a neutral equivalent of 187. The molecular weight as determined in benzene was 366 (calcd. 372) which together with the neutral equivalent showed it to be a diacid base.

The yields, melting points and analytical data of the products obtained from the reaction of piperidine and ethyl α-bromobenzoylacetate and ethyl α-bromo-α-benzoylpropionate are summarized in the following table.

| Compound, ethyl ( )-dipiperidino-benzoyl- | Yield,[a] % | M. p., °C. | Analyses, % Calcd. C | Calcd. H | Calcd. N | Found C | Found H | Found N |
|---|---|---|---|---|---|---|---|---|
| α,α-acetate | 39 | 131–132 | 70.31 | 8.37 | 7.82 | 70.14 | 8.31 | 7.37 |
| α,β-propionate | 28 | 132–133 | 70.95 | 8.60 | 7.52 | 70.60 | 8.64 | 7.91 |

The unbrominated esters, ethyl benzoylacetate and ethyl α-benzoylpropionate, were prepared in yields of 30 and 35%, respectively.[a] based on the amounts of bromo ester put into the reaction.

[a] Based on the amount of bromo ester put into the reaction.

In the case of ethyl α-bromo-α-phenylbenzoylacetate a solution of 22.1 g. (1 mol) of the bromo ester and 16 g. (3 mols) of piperidine in 300 cc. of ether was stirred in a

[11] Wahl, *Bull. soc. chim.*, [4] **1**, 461 (1907).

flask at room temperature for seven hours under a reflux condenser. No apparent reaction could be detected. The flask was placed on a steam-bath, the ether distilled and the residue heated for two hours. It was again taken up in ether and the precipitated piperidine hydrobromide removed by filtration. The yield of this salt was 10 g. (representing 95% of the bromine in the original bromo ester). The solution was washed with dilute sulfuric acid and then with dilute potassium carbonate. The ether solution was dried, the ether removed by distillation, and the residue fractionated. This fractionation yielded 1.7 g. of ethyl α-phenylbenzoylacetate, m. p. 89–90°, 6 g. of ethyl benzoate and 2–3 g. of ethyl phenylacetate. The two latter esters were mixed when distilled. They were identified by hydrolysis and fractional crystallization of the acids from water. The yield of ethyl benzoate was calculated from the amount of benzoic acid obtained. The residue from the distillation of the above esters was hydrolyzed with 30% potassium hydroxide and the mixture steam distilled. A small quantity of piperidine was obtained. This yield of piperidine from the hydrolysis of the residue indicated that amide formation had taken place in the reaction mixture. Amide formation was demonstrated by the fact that when 5 g. of the unbrominated ester was heated with 5 g. of piperidine on the steam-bath for two hours without a solvent and the reaction mixture worked up in the same manner as that described above, 1.2 g. of a mixture of ethyl benzoate and ethyl phenylacetate was obtained. Hydrolysis of the residue from the distillation with 30% potassium hydroxide gave 0.3 g. of piperidine after steam distillation. This yield represents 20% of amide formation.

## Summary

The reactions of piperidine with ethyl α-bromobenzoylacetate, ethyl α-bromo-α-benzoylpropionate and ethyl α-bromo-α-phenylbenzoylacetate have been studied. In the case of each of the first two of these bromo esters the unbrominated ester and a dipiperidino compound were the reaction products. The former product results from the brominating action of the bromo ester while the formation of the latter product is best explained as a secondary reaction product resulting from the action of the brominated piperidine on the normal reaction product of piperidine and a secondary or tertiary bromide. Ethyl α-bromo-α-phenylbenzoylacetate, a tertiary bromide which cannot lose hydrogen bromide, reacts only as a brominating agent since the unbrominated ester and its cleavage products were the only products obtained from the reaction of this bromo ester with piperidine.

Improved methods are given for the preparation of cyanodesoxybenzoin and ethyl α-phenylbenzoylacetate. The following compounds have been prepared and described for the first time: ethyl α-bromobenzoylacetate, ethyl α-bromo-α-benzoylpropionate, ethyl α-bromo-α-phenylbenzoylacetate, ethyl α,α-dibromobenzoylacetate, ethyl α,α-dipiperidinobenzoylacetate and ethyl α,β-dipiperidino-α-benzoylpropionate.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

# MIXED CATALYSTS IN THE FRIEDEL AND CRAFTS REACTION. THE YIELDS IN TYPICAL REACTIONS USING FERRIC CHLORIDE–ALUMINUM CHLORIDE MIXTURES AS CATALYSTS

BY W. A. RIDDELL AND C. R. NOLLER

RECEIVED AUGUST 12, 1931 PUBLISHED JANUARY 7, 1932

In a preliminary paper[1] it was shown that the yield of benzophenone from benzoyl chloride and benzene is practically a straight line function between pure ferric chloride and pure aluminum chloride. Boswell and McLaughlin[2] had found that the amount of hydrogen chloride evolved in the reaction of benzene with chloroform[3] was a maximum when an equimolecular mixture of ferric chloride and aluminum chloride was used, and Whitby and Gallay[4] that the yields of *o*-benzoylbenzoic acid from phthalic anhydride and benzene using one mole of ferric chloride and one mole of aluminum chloride were higher than the mean of those obtained using pure aluminum chloride and pure ferric chloride. We have now completed an investigation of a number of typical Friedel and Crafts reactions and have been able to make several generalizations in regard to the effect of varying the ratio of ferric chloride to aluminum chloride on the yields of the desired product.

## Experimental

In most cases an excess of benzene was used as solvent and the general procedure was the same as given in the previous paper,[1] the chief difference being that a simple mixture of the powdered chlorides was used instead of a fused mixture. A number of experiments showed that fused and unfused mixtures gave the same results. Because of the larger amount of catalyst required in the case of anhydrides, 100 cc. of benzene was used instead of the usual 70 cc. in order to get satisfactory stirring. The time of refluxing of the reaction mixture was kept constant throughout a run but varied with the different reactions and was in all cases one hour after all visible evolution of hydrogen chloride had stopped. If the product could be readily distilled at atmospheric pressure the yield was based on distilled

[1] Riddell and Noller, THIS JOURNAL, **52**, 4365 (1930).

[2] Boswell and McLaughlin, *Can. J. Res.*, **1**, 400 (1929).

[3] This reaction is not very satisfactory for a study of this kind, particularly when the amount of hydrogen chloride evolved is taken as a measure of the extent of the reaction taking place. In the first place the amount of hydrogen chloride evolved often bears little relation to the amount of the desired product that is formed [cf. Rubidge and Qua, THIS JOURNAL, **36**, 732 (1914)], and in the second place ferric chloride is known to have a chlorinating action on triphenylmethane, the main product of the reaction [Meissel, *Ber.*, **32**, 2422 (1899)].

[4] Whitby and Gallay, *Can. J. Res.*, **2**, 31 (1930).

product boiling over a suitable range. In other cases it was found that the results could be more easily reproduced by heating the product to 160° at 25 mm. and weighing the residue. The product was in all cases finally distilled to show its purity. As the proportion of ferric chloride increased, the isolation of the product became more difficult because of the presence of tarry by-products.

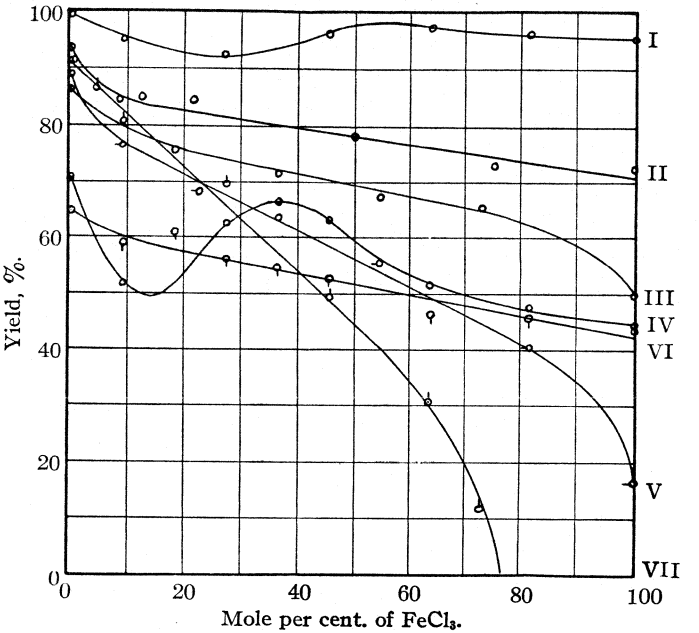



Fig. 1.—Reactions requiring 1 mole of catalyst: I, phenyl-*p*-tolylsulfone from *p*-toluenesulfonyl chloride and benzene; II, benzophenone from benzoyl chloride and benzene; III, *n*-butyrophenone from *n*-butyryl chloride and benzene; IV, triphenylcarbinol from carbon tetrachloride and benzene; V, *n*-propiophenone from *n*-propionyl chloride and benzene; VI, acetophenone from acetyl chloride and benzene; VII, benzophenone from benzene and excess carbon tetrachloride.

In the series on the preparation of benzophenone from carbon tetrachloride, excess carbon tetrachloride (70 cc.) was used as a solvent and the entire reaction run at 5–10.° Several series were also run using equivalent amounts of reactants and 100–150 cc. of carbon disulfide as a solvent. All the results are summarized in the curves of Figs. 1, 2 and 3.

## Discussion

Before beginning work on the mixed catalysts, the amount of pure aluminum chloride necessary to give the highest yield was determined. It is quite generally known that one mole of aluminum chloride ($AlCl_3$) is

required for each mole of acid chloride used, and two moles per mole of acid anhydride. We have found that in all cases studied the yield is directly proportional to the amount of catalyst up to these optimum amounts. A point that does not seem to have been previously recorded is that the yield rapidly falls off when more than these optimum amounts are used. We have also found that the reaction of benzene with excess carbon tetrachloride to give diphenyldichloromethane and of carbon tetrachloride with excess benzene to give triphenylchloromethane both require one mole of catalyst even though no oxygen compounds are involved. The reaction of benzoyl chloride and benzene using varying amounts of pure ferric

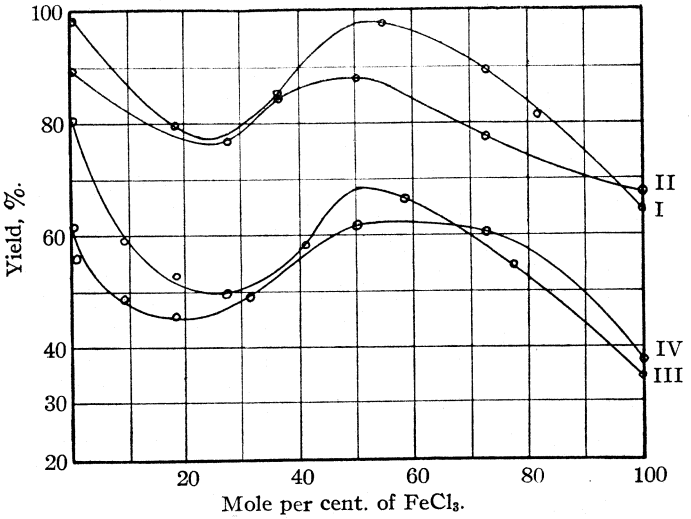



Fig. 2.—Reactions requiring 2 moles of catalyst: I, *n*-butyrophenone from *n*-butyric anhydride and benzene; II, benzophenone from benzoic anhydride and benzene; III, *n*-propiophenone from *n*-propionic anhydride and benzene; IV, acetophenone from acetic anhydride and benzene.

chloride likewise gives the maximum yield when one mole of ferric chloride per mole of acid chloride is used. Accordingly in all of the work on mixed catalysts 1.1 mole of catalyst was used per mole of acid chloride and 2.2 moles per mole of acid anhydride.

In the curves, the percentage yield is plotted against the mole per cent. of ferric chloride. It is readily seen that the curves are in general of two types: (1) those in which the yield is decreased in proportion to the amount of ferric chloride present[5] and (2) those in which the yield decreases rapidly

[5] Most of these curves show an initial rapid drop, a point which was discussed in the previous paper. The rapid drop as pure ferric chloride is approached is without doubt due to the difficulty of working up the reaction mixture because of the increased amount of tarry by-products.

to a minimum, then rises to a maximum and finally falls off to the value obtained with pure ferric chloride. To the first group belong the reactions of all the carboxylic acid chlorides with benzene and of benzene with an excess of carbon tetrachloride. In the latter case the ferric chloride is entirely non-reactive, probably because of the low temperature at which the reaction is carried out, and the curve is essentially the same as that obtained when pure aluminum chloride is used and the amount of catalyst is decreased. To the second group belong the reactions of all the acid anhydrides, of *p*-toluene sulfonyl chloride and of carbon tetrachloride with excess benzene.

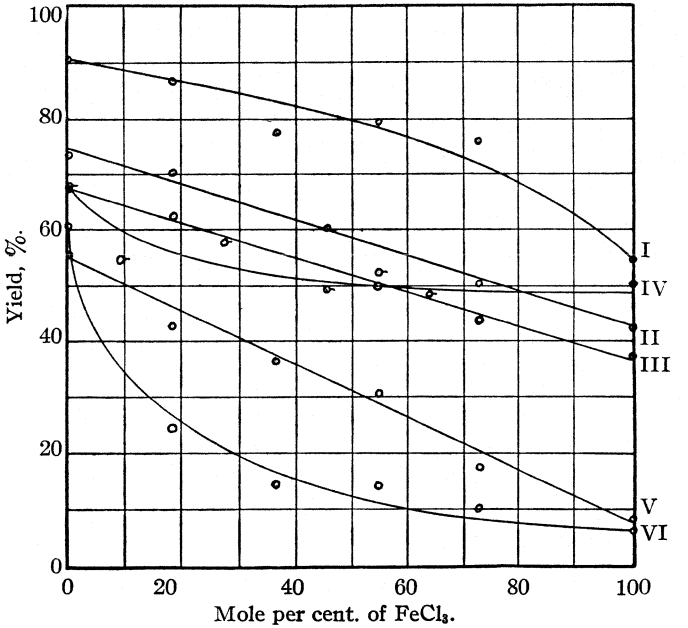



Fig. 3.—Reactions run in carbon disulfide: I, *p*-methoxyacetophenone from acetic anhydride and anisole; II, *p*-methoxyacetophenone from acetyl chloride and anisole; III, acetophenone from acetyl chloride and benzene; IV, acetophenone from acetic anhydride and benzene; V, *p*-bromoacetophenone from acetyl chloride and bromobenzene; VI, *p*-bromoacetophenone from acetic anhydride and bromobenzene.

It is quite difficult to explain the curves of the second type. In the first place this type occurs whether one or two moles of catalyst is required per mole of reactant. While we have found no exceptions to the rule that carboxylic acid chlorides give curves of the first type and acid anhydrides give curves of the second type, *p*-toluene sulfonyl chloride is an acid chloride and carbon tetrachloride is not an anhydride and yet both

give curves of the second type. The maximum in the curves of the second type appears to come in the majority of cases at fifty mole per cent. of ferric chloride and in most cases is almost equal to the yield obtained with pure aluminum chloride. In the case of carbon tetrachloride with excess benzene, however, the maximum comes at about thirty-five mole per cent. The maximum is quite sharp in all cases except that of acetic anhydride, where it is rather flat with little variation in yield while the amount of ferric chloride changes from fifty to seventy mole per cent. The minimum in the curves is in the neighborhood of twenty-five mole per cent. of ferric chloride and is always somewhat higher than the yield with pure ferric chloride.

If compound formation between the aluminum and ferric chlorides is to be considered as a possible explanation of the above results, it is almost necessary to assume the formation of two compounds, one composed of twenty-five mole per cent. of ferric chloride, which gives rather poor yields of product, and one composed of fifty mole per cent. of ferric chloride which gives yields almost as good as pure ferric chloride. This does not seem to be a very plausible assumption. Moreover, attempts were made to determine by the fusion point method whether compound formation between ferric and aluminum chlorides takes place and no evidence for it could be obtained. These results obtained at relatively high temperatures do not of course entirely eliminate the possibility of compound formation at the temperatures at which the Friedel and Crafts reaction takes place.

The results obtained when carbon disulfide was used as a solvent appear to further complicate the situation. These experiments, which were undertaken to determine the behavior of aromatic compounds other than benzene, show that in carbon disulfide solution neither acid chlorides nor acid anhydrides give the typical minimum–maximum curve within the limits of experimental error.

## Summary

The yields of product in a number of typical Friedel and Crafts reactions have been determined for various mixtures of anhydrous ferric chloride and aluminum chloride as catalysts. It was found that when excess benzene is used as a solvent, the reactions are of two types: (1) those in which the decrease in yield is proportional to the amount of ferric chloride added and (2) those in which the yield first decreased, then rose to a maximum at about fifty mole per cent. ferric chloride and then decreased to the yield with pure ferric chloride. It was further found that all reactions appear to be of the first type when run in carbon disulfide.

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

# ALIPHATIC DIAZO COMPOUNDS. A STABLE CRYSTALLINE OPTICALLY ACTIVE DIAZO COMPOUND

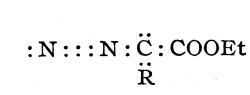
BY FRANCIS EARL RAY

RECEIVED AUGUST 13, 1931 PUBLISHED JANUARY 7, 1932

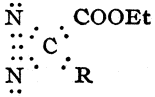
Optically active diazo esters containing but one possible asymmetric carbon atom bound to the diazo group have been prepared by Levene and Mikeska,[1] and Chiles with Noyes[2] and formula I has been assigned to these compounds. The specific rotations reported, however, have been very small, of the order of one or two degrees. This small rotation together with the fact that these compounds were liquids has evoked the criticism that impurities might be the cause of the observed rotation.

Large rotations were observed in the compounds prepared by Kendall and Noyes,[3] and Heubaum and Noyes.[4] Unfortunately these compounds contained another asymmetric carbon atom and were so unstable that no direct evidence could be obtained of the activity of the carbon atom adjacent to the diazo group. Ray,[5] from a study of the decomposition of Kendall and Noyes' methyl-γ-diazocamphonanate, concluded that the diazo group of this compound was active to the extent of about 5%.

On the other hand, the results of parachor measurements point to a ring structure, II, for the diazo esters. Analogous boiling points are adduced by Sidgwick[6] as further evidence for the ring structure.



I



II

In an effort to reconcile these divergent viewpoints Lindemann[7] and Ray[5] considered that formulas I and II represented tautomeric forms. If this is the case, racemization of the active form should occur until finally no activity would be observed. It seemed, therefore, of considerable interest to synthesize a stable, optically active, crystalline diazo compound containing but one asymmetric carbon atom. This has now been successfully accomplished by the preparation of β-naphthol-phenyldiazomethane, IV, from the active forms of the amine.

The straight chain formula, I, of the diazo compounds contains two free

[1] Levene and Mikeska, *J. Biol. Chem.*, **45**, 592 (1921); **52**, 485 (1922).

[2] Chiles with Noyes, THIS JOURNAL, **44**, 1798 (1922).

[3] Kendall and Noyes, THIS JOURNAL, **48**, 2404 (1926).

[4] Heubaum and Noyes, *ibid.*, **52**, 5070 (1930).

[5] Ray, *ibid.*, **52**, 3004 (1930).

[6] Sidgwick, *J. Chem. Soc.*, 1108 (1929).

[7] Lindemann, Wolter and Groger, *Ber.*, **63**, 702 (1930).

electrons on the asymmetric carbon atom. The presence of this pair of unshared electrons made it seem probable that an increase in negativity of the other groups would draw these electrons closer to the asymmetric carbon and contribute to the stability of the diazo compound. This proved to be the case.

The well-known negative character of the benzenoid rings suggested their use. Betti[8] prepared β-naphthol-phenylaminomethane some years ago and resolved it into its enantiomorphous forms and it was this compound from which the optically active diazo compound here described was prepared.

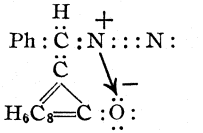
The β-naphthol-phenyldiazomethane was prepared from the active amine by treatment with nitrous acid. The light lemon-yellow compound resulting melted with vigorous decomposition at 120° and analyzed correctly. It was optically active, $[\alpha]_D^{30} = 420°$, and was stable to dilute acids at room temperatures. On boiling with acids the ketazine melting at 182° was obtained. Treatment with alkali gave a brightly colored orange-red salt which decomposed with explosive violence when heated. This salt retained its optical activity.[9] No change in rotation of an alcoholic solution could be observed after standing at room temperature (25–30°) for two weeks.

ROTATORY DISPERSION

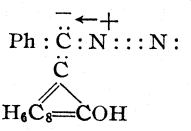
| λ | $[\alpha]^{30}$ | $[\alpha]^{30}$ | |
|---|---|---|---|
| 656.3 | − 310 | +285 | Red |
| 589.3 | − 420 | +405 | Yellow |
| 546.3 | − 518 | | Green |
| 486.1 | − 784 | | Blue |
| 435.8 | −1357 | | Violet |

The high specific rotation of this diazo compound combined with the fact that it contains but the one asymmetric carbon atom proves beyond doubt that the carbon atom connected with the diazo group may retain its asymmetry.

There is, nevertheless, an interesting possibility existing due to the presence of the naphtholic group in the molecule. Instead of the pentad nitrogen losing an electron to the carbon atom, IV, it is possible for this electron to be transferred to the oxygen, III. This would form a ring held together by a single polar valence between nitrogen and oxygen.



III



IV

[8] Betti, *Gazz. chim. ital.*, **31**, I, 386 (1901); **36**, II, 392 (1906).

[9] An intense violet coloration was obtained in the test for the naphtholic group with the reagent of Folin and Dennis, *J. Biol. Chem.*, **12**, 240 (1912).

If, however, a cyclic structure, III, is postulated, salt formation would destroy the ring and racemize the compound. That treatment with alkali does *not* racemize the compound must be accepted as evidence for the straight chain formula, IV. In addition, a quinoid structure is definitely eliminated by the optical activity of the compound. Staudinger[10] considers all the "so-called" diazo anhydrides to have the straight chain structure. He cites examples of several equally stable diazo compounds which contain only carbon, hydrogen and nitrogen.

The study of this and related compounds is being continued.

## Experimental Part

**β-Naphthol-phenylaminomethane** was prepared and resolved according to Betti's method.[8] Both the *d* and *l* forms melted at 137° and gave for one gram in 50.0 cc. of ether in a one decimeter tube: $\alpha_D \pm 1.20°$, $[\alpha]_D^{30} \pm 60.0 \pm 0.2°$.

*Anal.* Calcd. for $C_{17}H_{15}ON$: N, 5.62. Found: N, 5.67.

**β-Naphthol-phenyldiazomethane.**—Five grams of the active amine was dissolved in 50.0 cc. of pyridine, the equivalent amount of aqueous sodium nitrite was added, and the solution so obtained was slowly added to an excess of concentrated hydrochloric acid cooled in a freezing mixture.[11] The diazo compounds separate in light flaky lemon-yellow crystals melting with decomposition at 120°. It may be recrystallized from a mixture of ether and ligroin but if the diazotization is properly carried out a pure compound results. Sometimes considerable quantities of the ketazine are formed. For some undiscovered reason the *d* diazo compound was never obtained in quite as pure a state as the *l* isomer.

*Anal.* Calcd. for $C_{17}H_{12}ON_2$: H, 4.65; C, 78.43; N, 10.8. Subs., (*d*) 0.1117: $H_2O$, 0.0488; $CO_2$, 0.3191. Found: H, 4.89; C, 77.9; N, 10.6. Subs., (*l*) 0.1112, 0.1495: $H_2O$, 0.0473, 0.0649; $CO_2$, 0.3183, 0.4289. Found: H, 4.76, 4.86; C, 78.1, 78.2; N, 10.8.

Rotation (*d*): 1.000 g. in 100.0 cc. 95% alcohol–acetone, 80–20, at 30° in a one-decimeter tube:

$$\alpha_{656.3} +2.85°,\ \alpha_D +4.05°,\ [\alpha]_{656.3}^{30} +285°,\ [\alpha]_D^{30} +405°$$

Rotation (*l*): 1.000 g. in 100.0 cc. 95% alcohol–acetone, 80–20, at 30° in a one-decimeter tube:

$\alpha_{656.3} -3.10°$, $\alpha_D -4.20°$, $\alpha_{546.3} -5.18°$, $\alpha_{486.1} -7.84°$, $\alpha_{435.8} -13.57°$, $\pm 0.02°$, $[\alpha]_{656.3}^{30} -310°$, $[\alpha]_D^{30} -420°$, $[\alpha]_{546.3}^{30} -518°$, $[\alpha]_{486.1}^{30} -784°$, $[\alpha]_{435.8}^{30} -1357°$

**β-Naphtholphenoneketazine.**—On heating the diazo compound to 125° until evolution of nitrogen ceased, or by boiling with dilute acids, the ketazine was obtained. It was recrystallized from alcohol and melted at 182°. Of a light color when first prepared, it soon darkened to a yellowish or reddish-brown. Imperfect diazotization also resulted in the ketazine.

*Anal.* Calcd. for $C_{34}H_{24}O_2N_2$: N, 5.69. Found: N, 5.5, 5.4.

**Salt Formation.**—Alcoholic 1% solutions of the active *d* compound were treated with approximately one, two and three equivalents, respectively, of 25% potassium hydroxide. Some heat was liberated and the solutions darkened considerably. No lowering in the rotation was observed. In fact a small increase seemed observable

[10] Staudinger, *Ber.*, **49**, 1884, 1928 (1916).

[11] Krishna and Bhatia, Proc. 15th Indian Sci. Congress, 1928, p. 152.

but this may have been due entirely to the darkened solution; original $\alpha_D$ +4.05°; after treatment with alkali: $\alpha_D$ +4.10°, 4.15°, 4.12°; average, +4.12°.

**Racemization.**—An alcoholic 1% solution of the *l* compound was heated on the water-bath at 60–65° for four hours, alcohol being added to maintain the original volume. No evolution of gas was observed; original $\alpha_D$ −4.20°; after heating, $\alpha_D$ −3.72°, a decrease of about 12%. The compound is thus somewhat stable optically. Heating to boiling caused some decomposition to the ketazine.

## Summary

A stable, optically active, crystalline aliphatic diazo compound, β-naphthol-phenyldiazomethane, melting at 120° and having a high specific rotation, $[\alpha]_D^{30}$ ±420°, has been prepared. The rotatory dispersion is rather high, approximately 1000° between the red and violet.

On decomposition by heat or acids it forms the ketazine melting at 182°.

This shows conclusively that a carbon atom attached to the diazo group may retain its asymmetry.

CINCINNATI, OHIO

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[CONTRIBUTION FROM THE PLAUT RESEARCH LABORATORY OF LEHN & FINK, INC.]

# BACTERICIDAL PROPERTIES OF MONOETHERS OF DIHYDRIC PHENOLS. II. THE MONOETHERS OF HYDROQUINONE

BY EMIL KLARMANN, LOUIS W. GATYAS AND VLADIMIR A. SHTERNOV

RECEIVED AUGUST 13, 1931 PUBLISHED JANUARY 7, 1932

It has been shown in the preceding communication (Part I of this series) that among the monoethers of resorcinol there are a number of compounds which show very considerable bactericidal potency as determined with *B. typhosus* and *Staphylococcus aureus* as test organisms.[1] This bactericidal efficacy was found to depend particularly upon the length of the chain and the molecular weight of the substituting aliphatic or aromatic radical.

Continuing this series of investigations, we prepared several monoethers of hydroquinone in order to study the antibacterial effect of replacing the hydrogen atom of one hydroxyl group of this dihydric phenol by an organic radical.

## Discussion

The number of hydroquinone monoethers described in the literature is comparatively small, and none appear to have been tested for their effect upon bacteria. Hydroquinone itself and some of its nucleus substituted derivatives were studied by several investigators with the aid of certain common pathogenic microbes. Thus Cooper and Woodhouse[2] found the phenol coefficient of hydroquinone to be 1.0 against *B. typhosus*, 1.1 against *Staphylococcus* and 0.96 against *B. coli*. Cooper and Forstner[3]

[1] E. Klarmann, L. W. Gatyas and V. A. Shternov, THIS JOURNAL, **53**, 3397 (1931).

[2] E. A. Cooper and D. L. Woodhouse, *Biochem. J.*, **17**, 600 (1923).

[3] E. A. Cooper and G. E. Forstner, *ibid.*, **18**, 940 (1924).

determined the growth-inhibiting concentrations of hydroquinone and some of its nucleus substituted homologs for *B. pyocyaneus* and *B. coli.* They found the growth of the former bacteria to be inhibited by the following dilutions: hydroquinone 1:2550, methylhydroquinone 1:1040, dimethylhydroquinone 1:1240 and thymohydroquinone 1:330. The corresponding bacteriostatic dilutions for *B. coli* were 1:710, 1:700, 1:1740 and 1:1100, respectively. Additional data on the antibacterial properties of hydroquinone may be found in the publications of Cooper,[4] Regenstein,[5] Morgan and Cooper,[6] Cooper and Haines[7] and others.

The compounds prepared and studied by us to date comprise the normal aliphatic saturated monoethers of hydroquinone up to the nonyl ether, some secondary ethers and a number of ethers obtained by substitution with aromatic groups. The bacteriological investigation was carried out with the aid of the two pathogenic bacteria used before, *viz.*, *B. typhosus* and *Staphylococcus aureus;* the reasons for their selection were given in our preceding paper. However, experiments with several other bacteria are under way at this time.

TABLE I

BACTERICIDAL ACTION OF MONOETHERS OF HYDROQUINONE

| | *B. typhosus* Bactericidal concentrations | | | | *Staph. aureus* Bactericidal concentrations | | | |
|---|---|---|---|---|---|---|---|---|
| | 5 min. | 10 min. | 15 min. | Phenol coeff. | 5 min. | 10 min. | 15 min. | Phenol coeff. |
| Hydroquinone | 1:1500 | <1:2000 | <1:2000 | >12 | 1:30 | 1:35 | 1:45 | 0.44 |
| Alkyl ethers | | | | | | | | |
| Methyl | 1:130 | 1:140 | 1:150 | 1.0 | 1:60 | 1:70 | 1:70 | 0.8 |
| Ethyl | 1:200 | 1:225 | 1:225 | 1.5 | 1:100 | 1:100 | 1:100 | 1.5 |
| *n*-Propyl | 1:700 | 1:750 | 1:750 | 5.4 | 1:275 | 1:300 | 1:325 | 4.1 |
| Isopropyl | 1:450 | 1:500 | 1:500 | 3.6 | 1:150 | 1:180 | 1:200 | 2.3 |
| *n*-Butyl | 1:1800 | 1:2000 | 1:2250 | 14 | 1:700 | 1:800 | 1:800 | 9.3 |
| *n*-Amyl | 1:3500 | 1:4000 | 1:4000 | 29 | 1:2250 | 1:2500 | 1:2500 | 30 |
| *sec.*-Amyl | 1:2500 | 1:2750 | 1:2750 | 19 | 1:2000 | 1:2000 | 1:2250 | 26 |
| *n*-Hexyl | 1:2500 | 1:2750 | 1:3250 | 18 | 1:7500 | 1:7500 | 1:7500 | 100 |
| *n*-Heptyl | 1:2250 | 1:2500 | 1:2500 | 17 | 1:13000 | 1:16000 | 1:20000 | 200 |
| *n*-Octyl | | | | | 1:30000 | 1:32500 | 1:32500 | 360 |
| Aromatic ethers | | | | | | | | |
| Phenyl | 1:5500 | 1:6000 | 1:7000 | 41 | 1:1800 | 1:2000 | 1:2000 | 28 |
| Benzyl | 1:2500 | 1:2750 | 1:3000 | 21 | 1:1000 | 1:1100 | 1:1200 | 14 |
| Phenylethyl | 1:3500 | 1:3500 | 1:3750 | 25 | 1:2250 | 1:2250 | 1:2500 | 29 |
| Phenylpropyl | 1:1400 | 1:1500 | 1:1500 | 10 | 1:1200 | 1:1400 | 1:1500 | 13 |
| Control | | | | | | | | |
| Phenol (average) | 1:130 | 1:140 | 1:160 | 1 | 1:70 | 1:80 | 1:90 | 1 |

The bactericidal effectiveness of the monoethers of hydroquinone appears from Table I and the two graphs. The minimum bactericidal concentrations were determined for periods of exposure of five, ten and fifteen

[4] E. A. Cooper, *British Medical J.*, I, 1234, 1293, 1359 (1912).

[5] H. Regenstein, *Zentr. Bakteriologie I*, Orig., **63**, 281 (1912).

[6] G. T. Morgan and E. A. Cooper, *Biochem. J.*, **15**, 587 (1921).

[7] E. A. Cooper and R. B. Haines, *J. Hygiene*, **28**, 163 (1928).

minutes at 37° and the phenol coefficients were calculated from these data. As in the case of the resorcinol monoethers the series of compounds shows a different general behavior toward the two test organisms (incidentally of different Gram reaction). Thus the germ killing effect upon *B. typhosus* of the aliphatic derivatives increases from the methyl ether to the *n*-amyl ether, and then decreases again down to the *n*-heptyl derivative. In the case of *Staphylococcus aureus* a continuous rise is observed, the maximum being reached apparently with the *n*-octyl ether. No tests could be carried

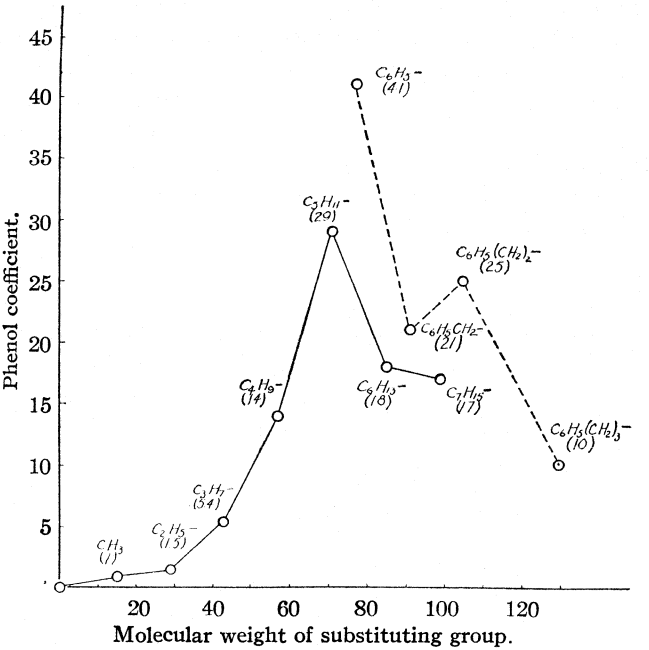



Fig. 1.—The effect of the substituting radical upon the bactericidal action of monoethers of hydroquinone; test organism, *B. typhosus:* full line ——— alkyl derivatives; dash line — — — aromatic derivatives.

out beyond the *n*-heptyl ether with *B. typhosus* and the *n*-octyl ether with *Staphylococcus aureus*, owing to the insolubility of the compounds and the resulting impossibility of preparing solutions of the required concentrations. Generally the bactericidal action of the aliphatic monoethers of hydroquinone is found to be less than that of the resorcinol monoethers, although some derivatives appear to be very potent bactericides, particularly for *Staphylococcus aureus*. As in the case of resorcinol derivatives, the monoethers of hydroquinone obtained by substitution with a secondary radical are less effective than the corresponding straight chain derivatives.

Introduction of aromatic groups also leads to strongly bactericidal com-

pounds. The potency of some of them compares favorably with that of the corresponding resorcinol monoethers. In both cases there is a drop in efficacy from the phenyl to the benzyl ether derivatives, then a rise with further increase of the molecular weight of the phenylalkyl group to the phenylethyl ether; but unlike the case of resorcinol, there is another decline of bactericidal potency in the hydroquinone phenylpropyl ether.

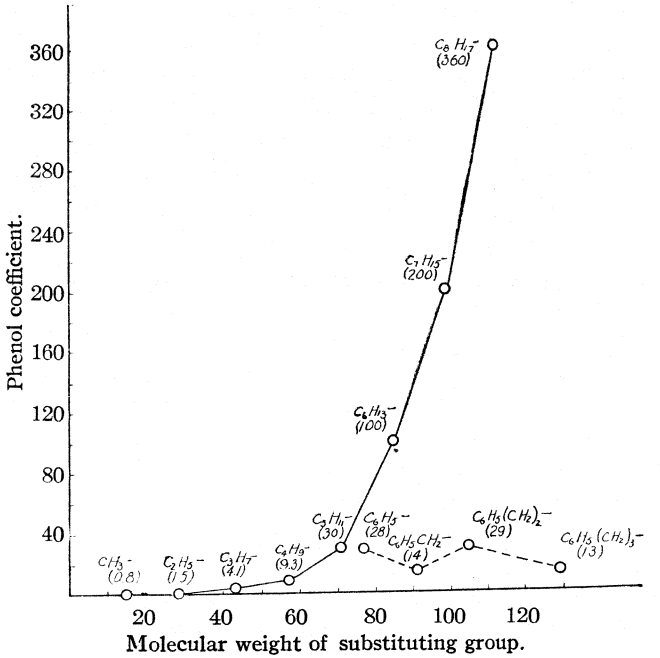



Fig. 2.—The effect of the substituting radical upon the bactericidal action of monoethers of hydroquinone; test organism, *Staph. aureus:* full line ——— alkyl derivatives; dash line — — — aromatic derivatives.

In contrast to resorcinol, the parent compound hydroquinone appears to be a more potent germicide for *B. typhosus* than some of its monoether derivatives. Undoubtedly this is due to the capacity of hydroquinone to act in certain cases not only as a phenol, but also as a powerful reducing agent, because of its ease of oxidation to benzoquinone. Besides, it is possible that the benzoquinone formed further acts on bacteria; Morgan and Cooper[6] attribute considerable germicidal potency to this compound. In contrast to this, the structural configuration of the monoethers of hydroquinone precludes the easy oxidation to benzoquinone derivatives; the ethers, therefore, may be expected to act upon bacteria as phenol derivatives, without any collateral action. This contention is also borne out by the consideration of the temperature coefficients

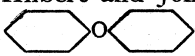
$$\left(\frac{\text{average min. bacteric. concn. at } 20°}{\text{average min. bacteric. concn. at } 37°}\right)$$

of the bactericidal action upon *B. typhosus* of hydroquinone on one hand, and of its ethers on the other, as shown in Table II.

TABLE II

| | Temp., °C. | *B. typhosus* Bactericidal concentrations 5 min. | 10 min. | 15 min. | Phenol coeff. | Temp. coeff. for 17° C. | *Staph. aureus* Bactericidal concentrations 5 min. | 10 min. | 15 min. | Phenol coeff. | Temp. coeff. for 17°C. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Hydroquinone | 20 | 1:100 | 1:100 | 1:200 | 1.4 | | 1:20 | 1:20 | 1:25 | 0.34 | |
| | 37 | 1:1500 | <1:2000 | <1:2000 | >12 | >15 | 1:30 | 1:35 | 1:45 | .44 | 1.7 |
| Hydroquinone methyl ether | 20 | 1:80 | 1:90 | 1:90 | 1.0 | | | | | | |
| | 37 | 1:130 | 1:140 | 1:150 | 1.0 | 1.6 | | | | | |
| Hydroquinone propyl ether | 20 | 1:450 | 1:550 | 1:600 | 6.1 | | 1:225 | 1:150 | 1:250 | 4.4 | |
| | 37 | 1:700 | 1:750 | 1:750 | 5.4 | 1.3 | 1:275 | 1:300 | 1:325 | 4.1 | 1.2 |

Thus at 20° the germicidal action of hydroquinone upon *B. typhosus* hardly exceeds that of phenol at the same temperature, while at 37° it is more than fifteen times greater than at 20° and more than twelve times greater than that of phenol at 37°. In contrast to this, an increase of temperature of 17° raises the bactericidal effect of the hydroquinone ethers studied to a much lesser extent. All of this indicates that in the case of the unsubstituted hydroquinone a rise in temperature not only increases what might be termed its antibacterial "phenol reactivity" against *B. typhosus* but even more so, intensifies another, collateral effect. *Staphylococcus aureus* apparently is not susceptible to this "collateral" action, and in this case the unsubstituted hydroquinone manifests a weaker antibacterial potency than its lowest monoether. Also a consideration of the temperature coefficient discloses nothing unusual here. Future experiments will have to show whether there is a relation between this phenomenon and the Gram reaction.

Since the monophenyl ethers of the dihydric phenols may also be regarded as hydroxydiphenyl oxides, a comparison with the hydroxydiphenyl sulfides studied by Hilbert and Johnson[8] is of interest. The *p*-derivatives in question are  and 

A strict comparison is not feasible owing to differences in bacteriological testing methods, but the *p*-hydroxydiphenyl sulfide (with a *B. typhosus* phenol coefficient of 115) appears to be almost three times as potent as the corresponding oxide; the *m*-hydroxydiphenyl sulfide, however, is only somewhat over 50% more effective than the corresponding resorcinol phenyl ether.

The antibacterial superiority of the hydroxydiphenyl sulfides over the corresponding oxides is probably due to a better "lipoid" solubility of the former.

[8] G. E. Hilbert and T. B. Johnson, THIS JOURNAL, 51, 1526 (1929).

## Experimental Part

(a) **Chemical.**—The compounds of this series were prepared by a number of different methods. Most of them were obtained by condensation of hydroquinone with an organic halide. This condensation was carried out either directly, or in the presence of potassium hydroxide or carbonate. The hydroquinone monophenyl ether (*p*-hydroxydiphenyl oxide) was prepared by condensation of *p*-bromophenol with phenol in the presence of potassium hydroxide since the bromine atom in bromobenzene is too firmly attached to the nucleus to react with hydroquinone directly.

The analytical properties of the hydroquinone monoethers prepared are given in Table III.

TABLE III

ANALYTICAL DATA OF MONOETHERS OF HYDROQUINONE

| Alkyl Ethers | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | M. p., °C. | B. p., °C. | mm. |
|---|---|---|---|---|---|---|---|---|
| Ethyl[a] | $C_8H_{10}O_2$ | 69.54 | 69.39 | 7.30 | 7.44 | 65–66 | | |
| *n*-Propyl | $C_9H_{12}O_2$ | 71.01 | 71.28 | 7.95 | 7.91 | 56–57 | | |
| Isopropyl | $C_9H_{12}O_2$ | 71.01 | 71.70 | 7.95 | 8.15 | | 117 | 4 |
| *n*-Butyl | $C_{10}H_{14}O_2$ | 72.26 | 72.31 | 8.49 | 8.75 | 64–65 | | |
| *n*-Amyl | $C_{11}H_{16}O_2$ | 73.31 | 73.75 | 8.95 | 9.07 | 49–50 | | |
| *Sec.*-amyl | $C_{11}H_{16}O_2$ | 73.31 | 73.77 | 8.95 | 8.87 | 48–49 | | |
| *n*-Hexyl | $C_{12}H_{18}O_2$ | 74.20 | 74.02 | 9.34 | 9.36 | 48 | | |
| *n*-Heptyl | $C_{13}H_{20}O_2$ | 74.98 | 75.57 | 9.68 | 10.20 | 60 | | |
| *n*-Octyl | $C_{14}H_{22}O_2$ | 75.65 | 75.47 | 9.98 | 9.83 | 60–61 | | |
| *n*-Nonyl | $C_{15}H_{24}O_2$ | 76.22 | 76.25 | 10.24 | 10.14 | 68.5 | | |
| **Aromatic ethers** | | | | | | | | |
| Phenyl[b] | $C_{12}H_{10}O_2$ | 77.43 | 73.32 | 5.42 | 5.31 | 83 | | |
| Benzyl[c] | $C_{13}H_{12}O_2$ | 78.01 | 77.91 | 6.05 | 6.32 | 121 | | |
| Phenylethyl | $C_{14}H_{14}O_2$ | 78.48 | 77.90 | 6.59 | 6.72 | | 183 | 4 |
| Phenylpropyl | $C_{15}H_{16}O_2$ | 78.92 | 78.24 | 7.07 | 7.10 | 75–76 | | |

[a] Previously prepared by Wichelhaus, *Ber.*, **12**, 1501 (1879); Hantzsch, *J. prakt. Chem.*, [II] **22**, 462 (1880). [b] Previously prepared by Häussermann and Bauer, *Ber.*, **29**, 2085 (1896); Mueller, *ibid.*, **34**, 1070 (1901). [c] Previously prepared by Schiff and Pelizzari, *Ann.*, **221**, 369 (1883).

The methods applied in the preparation of the hydroquinone monoethers are illustrated in the following examples.

**Direct Condensation. Preparation of *p*-Hydroxyphenyl Benzyl Ether.**—To a boiling solution of 45.5 g. (10% excess) of hydroquinone in 200 cc. of xylene, 47.5 g. of benzyl chloride was added drop by drop in the course of six hours. Hydrogen chloride fumes escaped during the process. The mixture was allowed to cool. It was diluted with ether and washed with water, then shaken repeatedly with a 10% solution of potassium hydroxide. The combined alkaline extracts were washed with ether and acidified with dilute hydrochloric acid. A crystalline precipitate of *p*-hydroxyphenyl benzyl oxide formed. It was filtered off and purified by crystallization from water.

The same compound was also obtained by condensation in acetone solution in the presence of potassium carbonate.

The hydroquinone dibenzyl ether which forms at the same time was isolated from

the ether solution after extraction with alkali, and purified by crystallization from alcohol. It melts at 127–128° (uncorr.).

*Anal.* Calcd. for $C_{20}H_{18}O_2$: C, 82.76; H, 6.21. Found: C, 82.54; H, 6.39.

**Condensation in the Presence of Potassium Hydroxide. Preparation of *p*-Hydroxyphenyl Monoisopropyl Ether.**—Hydroquinone (37 g.) was dissolved in 40 cc. of alcohol. To this solution 56.7 g. of isopropyl iodide was added. A solution of 20 g. of potassium hydroxide in 60 cc. of water was added under reflux drop by drop in the course of one hour, and boiling continued for another three hours. An excess of alkali was added and the resulting mixture was steam distilled in order to remove the unconverted isopropyl iodide and the di-isopropyl ether of hydroquinone. The solution was acidified with hydrochloric acid and the steam distillation continued whereby the desired hydroquinone monoisopropyl ether was driven out. It was isolated from the distillate by extraction with ether, and after evaporation of the ether it was purified by repeated distillation in a vacuum.

The isolation of monoethers by distilling with ordinary steam cannot be applied conveniently in the case of the ethers containing a substituting group with more than four carbon atoms. Therefore, in the case of the butyl and higher ethers, the separation of the di-ether from the mono-ether was accomplished with the aid of alkali in the manner described under the preparation of the benzyl ether.

The lower aliphatic ethers which are solid at room temperature were crystallized from water, the higher ones (from the amyl ether upward) from ligroin (boiling range 60–70°).

Hydroquinone monophenylethyl ether was prepared by the condensation of hydroquinone with phenylethyl bromide in the presence of dilute potassium hydroxide as described above. After isolation by the alkali method it was purified by repeated vacuum distillation.

A number of aliphatic di-ethers which formed simultaneously in the course of the processes aiming at the preparation of the monoethers, were prepared in a pure state (by crystallization from alcohol). They are: hydroquinone diethyl ether, m. p. 70–71°. Calcd. for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.46; H, 8.54. Hydroquinone dibutyl ether, m. p. 45–46°. Calcd. for $C_{14}H_{22}O_2$: C, 75.67; H, 9.91. Found: C, 75.82; H, 9.95. Hydroquinone di-isoamyl ether, m. p. 58–59°. Calcd. for $C_{16}H_{26}O_2$: C, 76.80; H, 10.40. Found: C, 76.74; H, 10.56.

**Preparation of *p*-Hydroxydiphenyl Oxide.**—While this compound has been obtained previously by diazotization of the *p*-aminodiphenyl ether we secured it by a direct condensation of *p*-bromophenol with phenol in the presence of alkali and copper.

Phenol (47 g., *i. e.*, 100% excess) and potassium hydroxide (15 g.) were placed in a round-bottomed flask and heated in an oil-bath until the water was driven off. The mixture was allowed to cool and 43.5 g. of *p*-bromophenol and 0.2 g. of freshly precipitated copper were added. The flask was connected with a reflux condenser and an inlet tube for hydrogen. While a continuous current of hydrogen was allowed to pass through the apparatus the temperature of the oil-bath was raised gradually to 130° and maintained for two hours. After cooling, the reaction mixture was diluted with water, acidified and distilled with steam in order to remove the unconverted bromobenzene and phenol. The solution was shaken with ether and after evaporation of the latter the residue was crystallized from a mixture of equal volumes of benzene and ligroin.

(b) **Bacteriological.**—The bacteriological testing technique was the same as outlined in the preceding publication of this series, except for the experiments carried out at the lower temperature.

Because of the difficult solubility, particularly of the higher ethers,

alcohol had to be used to facilitate solution. In most cases, however, not more than 10% of alcohol was present in the bactericidal dilutions given in Table I. Only with the heptyl and octyl ethers of hydroquinone were we compelled to have 15% of alcohol present, while the benzyl ether required 20% in the test with *Staphylococcus aureus*.

## Summary

The second report in the series of investigations on the bactericidal properties of monoethers of dihydric phenols, deals with the derivatives of hydroquinone. The compounds studied have been obtained by introduction of the following aliphatic and aromatic radicals: methyl, ethyl, *n*- and isopropyl, *n*-butyl, *n*- and *sec.*-amyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl; phenyl, benzyl, phenylethyl and phenylpropyl.

As in the case of the resorcinol monoethers, described in the preceding paper, a number of compounds of considerable germicidal potency are also found in the hydroquinone series; here, too, the molecular weight and the structure of the substituting radicals play a determining role. The two test microörganisms used in this investigation, *viz.*, *B. typhosus* and *Staphylococcus aureus*, show a different behavior toward these compounds, similar to that observed in the case of the resorcinol ethers. Thus in experiments with *B. typhosus* the bactericidal potency of the aliphatic monoethers increases with increasing molecular weight of the substituting group, reaching the maximum with the *n*-amyl ether and decreasing thereafter. In contrast to this the maximum effect upon *Staphylococcus aureus* is not reached with the *n*-octyl ether; an extension beyond this point was not feasible, for the time being, because of the insufficient solubility of the higher ethers.

In the case of the resorcinol monoethers the maximum of germicidal potency was shown by the hexyl ether, with *B. typhosus* as test organism while the effect upon *Staphylococcus aureus* did not reach a definite maximum with the nonyl ether.

The normal alkyl derivatives are more potent germicides than those containing secondary alkyl groups.

The monoethers of hydroquinone obtained by the introduction of aromatic groups are also powerful germicides. The phenyl ether (*p*-hydroxydiphenyl oxide) is most effective against *B. typhosus*, the phenylethyl ether against *Staphylococcus aureus*. The antibacterial action drops with the benzyl ethers, rises again with the phenylethyl ether, and decreases with the phenylpropyl ether. While the corresponding resorcinol monoethers were generally more effective, a similar behavior was observed except that the bactericidal action of the phenylpropyl ether upon *Staphylococcus aureus* surpassed that of the phenylethyl derivative.

BLOOMFIELD, NEW JERSEY

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

# THE ALKYLATION OF AMINES AS CATALYZED BY NICKEL

BY CHARLES F. WINANS AND HOMER ADKINS

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The catalytic hydrogenation of various nitrogen containing organic compounds such as primary arylamines, cyanides, oximes, anils, nitro and nitroso compounds often results in the formation of secondary and tertiary amines as well as of the desired primary amines. The further study of these processes seems worth while for several reasons: first, to ascertain how to exercise a better control of the competitive reactions, second because of the interest in the mechanisms of these transformations and third because of the paucity of available information as to reactions other than hydrogenation induced by nickel.

**Alkylation of Amines by Alcohols.**—Ethylcyclohexylamine was recently obtained in an excellent yield by the hydrogenation of aniline in an ethanol solution using nickel as a catalyst.[1] This result suggested that nickel is a catalyst for the reaction of amines with alcohols according to equation I

$$C_6H_{11}NH_2 + C_2H_5OH = C_6H_{11}NHC_2H_5 + H_2O \qquad (I)$$

This supposition has been confirmed by the fact that the reaction indicated does not occur to any appreciable extent if the reactants are heated at 200° in the absence of active nickel. However, when 0.55 mole of cyclohexylamine, 1.2 mole of ethanol and 4 g. of a nickel catalyst were heated under a pressure of 75 atmospheres of hydrogen at 200° for three and one-half hours, the fractionation of the products showed 8.6 g. of cyclohexylamine, 42.0 g. of ethylcyclohexylamine, 6 g. of diethylcylcohexylamine and 2.0 g. of dicyclohexylamine. If the reactants were heated at 150° with a nickel catalyst no reaction occurred, but at 175° only 52% of the cyclohexylamine was recovered unchanged. In general the same factors seem to govern the activity of nickel for the catalysis of the alkylation of amines as govern its activity for hydrogenation, since a preparation of catalyst which was rather inactive for hydrogenation was also rather inactive for alkylation.

Piperidine and α-methylpiperidine reacted with ethanol, butanol and cyclohexanol at 200° in a similar way, the yields of the corresponding tertiary amines being 76 to 80%. Mechanical losses account for about one-third of the remainder, while under the conditions used there was 13 to 17% of unreacted secondary amine. At temperatures lower than 165° piperidine and some of its derivatives do not react with ethanol in the presence of nickel. This is shown by the fact that recently α- and

[1] Adkins and Cramer, THIS JOURNAL, **52**, 4354 (1930).

β-pyridylphenylethylene and α-benzylpyridine were hydrogenated in ethanol solution at 150–165° to α- and β-piperidylphenylethane and α-benzylpiperidine without any appreciable amount of alkylation.[1]

Since the same yields of alkylated amine were obtained in an atmosphere of nitrogen as were obtained in an atmosphere of hydrogen it is obvious that the latter plays no part in the reaction.

Cyclohexylamine did not react to any appreciable extent with methanol, propanol-2 or ethylene glycol. Tertiary butyl alcohol did not react with piperidine, nor did ethanol react with aniline under the conditions used for the successful alkylations described above. β-Phenylethylamine reacted with butanol-1, as did amylamine with ethanol, but such a variety of products resulted that the method seems to have little preparational value.

**Alkylation of Amines by Amines.**—Rosenmund and Jordan,[2] and more recently Kindler,[3] showed that over palladium benzylamine and β-phenylethylamine in boiling xylene or alcohol were converted in excellent yields to the corresponding secondary amines with the evolution of ammonia. It has been found that nickel also catalyzes this type of alkylation under suitable conditions.

$$2C_6H_5CH_2CH_2NH_2 = (C_6H_5CH_2CH_2)_2NH + NH_3 \qquad (II)$$

Cyclohexylamine did not undergo reaction II rapidly but β-phenylethylamine was converted completely to di-β-phenylethylamine in three and one-half hours at 200° over a nickel catalyst. In a similar way *n*-amylamine was completely converted into di-*n*-amylamine. Aniline did not form diphenylamine under similar conditions.

It is noteworthy that the alkylation formulated in equation II proceeded only as far as the secondary amine, since no tertiary amine was isolated from any of the experiments referred to above. This behavior is in marked contrast to the alkylation of primary amines with alcohols, which usually results in the formation of some tertiary amine.

**Alkylation of Amines during Hydrogenation.**—Having as a background a knowledge of the conditions inducing the two types of alkylation of amines referred to above, it is possible to consider more conclusively the nature of the reactions which result in the formation of secondary and tertiary amines during the reduction of aryl amines, cyanides, etc. Under the most advantageous conditions so far used in this Laboratory for the hydrogenation of aniline there was produced 1 part of dicyclohexylamine for 9 parts of cyclohexylamine, while with less active catalysts (with a resultant longer period of hydrogenation) the proportion of the secondary amine was increased to 1 part for 2 parts of primary amine. Similarly in the hydrogenation of benzyl cyanide there was produced under the most advantageous conditions 1 part of di-β-phenylethylamine for 6 parts of

[2] Rosenmund and Jordan, *Ber.*, **58B**, 51 (1925).

[3] Kindler, *Ann.*, **485**, 113 (1931).

β-phenylethylamine, while in the hydrogenation of butyl cyanide the ratio of secondary to primary amine was 1 to 3. The formation of the secondary amine in the hydrogenation of aniline is certainly the result of an alkylation in the sense of equation II. However, this reaction cannot account for the formation of secondary amines in the hydrogenation of cyanides for reaction II did not occur at temperatures below about 160–170°, while the cyanides were hydrogenated at 125° or lower.

Mignonac[4] proposed the hypothesis that the formation of dibenzylamine in the hydrogenation of phenyl cyanide depended upon the intermediate formation of hydrobenzamide from benzalimine as shown in equations III to V.

$$RC{\equiv}N + H_2 \longrightarrow RCH{=}NH \quad \text{(III)}$$

$$3RCH{=}NH \longrightarrow RCH(N{=}CHR)_2 + NH_3 \quad \text{(IV)}$$

$$RCH(N{=}CHR)_2 + H_2 \longrightarrow RCH_2NH_2 + (RCH_2)_2NH \quad \text{(V)}$$

Rupe and Glenz[5] also postulated a compound of the hydrobenzamide type as an intermediate in the formation of secondary amines from cyanides although according to their scheme it results from the reaction of ammonia with an aldehyde produced by hydrolysis of an aldimine.

Von Braun[6] suggested that the formation of secondary amines in the hydrogenation of cyanides was due to the interaction of an aldimine (formed as in equation III) with a primary amine as shown in equations VI and VII, VIII (or VI and VIIa, VIIIa).

$$RCH{=}NH + H_2 = RCH_2NH_2 \quad \text{(VI)}$$

$$RCH{=}NH + RCH_2NH_2 = RCH{=}NCH_2R + NH_3 \quad \text{(VII)}$$

$$RCH{=}NCH_2R + H_2 = (RCH_2)_2NH \quad \text{(VIII)}$$

$$RCH{=}NH + RCH_2NH_2 = RCH(NH_2)NHCH_2R \quad \text{(VIIa)}$$

$$RCH(NH_2)NHCH_2R + H_2 = (RCH_2)_2NH + NH_3 \quad \text{(VIIIa)}$$

Kindler[3] considers that the aldimine is hydrolyzed to an aldehyde which then reacts with primary amine to give the anil which is hydrogenated to the secondary amine.

The formulations of Rupe and Glenz and of Kindler are of no significance in connection with the hydrogenations reported in this paper for our results were obtained in most cases under anhydrous conditions, although it was shown that the ratio of primary and secondary amines produced in the hydrogenation of benzyl cyanide was the same irrespective of whether or not water was present in the reaction medium.

The salient facts in regard to the mechanism of the reaction seem to be as follows:

1. Benzalimine (as the hydrochloride) reacts with aniline to give benzalaniline as indicated in equation VII for the reaction of an imine

[4] Mignonac, *Compt. rend.*, **171**, 114 (1930).

[5] Rupe and Glenz, *Helv. Chim. Acta*, **5**, 937 (1922).

[6] Von Braun, *Ber.*, **56**, 1988 (1923).

and an amine. This reaction was discovered by Busch[7] and has given a 67% yield of benzalaniline in this Laboratory.

2. Benzalaniline is almost quantitatively hydrogenated to the corresponding secondary amine.

3. Benzalimine reacts with itself to give hydrobenzamide as indicated in equation IV.

4. Hydrobenzamide upon hydrogenation gave a 94% yield of benzylamine and a 96% yield of dibenzylamine as calculated on the basis of equation V. Mignonac obtained much higher yields of dibenzylamine with corresponding lower yields of the primary amine. The results here reported are thus in better accord with his formulation than were his own experiments. This better agreement of experiment with hypothesis is no doubt due to the greater activity of our catalyst, which minimized the importance of side reaction.

5. Hydrobenzamide as shown by Busch and confirmed in this Laboratory is readily converted into benzalimine even at 5° according to equation XI.

$$C_6H_5CH(N{=}CHC_6H_5)_2 + 2C_2H_5OH + 2HCl = 2C_6H_5CH{=}NHHCl + C_6H_5CH(OC_2H_5)_2 \quad (XI)$$

The facts listed as 1 and 2 are in accord with von Braun's hypothesis as to the mechanism of the formation of secondary amines in the hydrogenation of cyanides, while facts 3 and 4 are in harmony with Mignonac's hypothesis. However, in view of fact 5 there seems to be no reason to assume that both a synthesis and a cleavage occur, such as is involved in the latter hypothesis. von Braun's hypothesis seems to be entirely adequate to explain the results obtained.

The above discussion of the reactions resulting in the formation of secondary amines in the hydrogenation of cyanides is also pertinent to the formation of secondary amines in the hydrogenation of oximes, nitro and nitroso derivatives, since highly reactive imines would also be formed in the course of these hydrogenations.

**Alkylation of Amines with Aldehydes and Ketones.**—Another method for the catalytic alkylation of ammonia and amines is that discovered by Mignonac[8] and applied among others by Skita and Kiel[9] and Manske and Johnson.[10] This method involves the reaction of an aldehyde or ketone with ammonia or an amine in a solvent followed immediately by hydrogenation. The method is illustrated in equations XII and XIII.

$$C_6H_{11}NH_2 + C_3H_7CHO = (C_3H_7CH(OH)NHC_6H_{11}) \text{ or } (C_3H_7CH{=}NHC_6H_{11} + H_2O) \quad (XII)$$

$$C_3H_7CH{=}NHC_6H_{11} + H_2 = C_4H_9NHC_6H_{11} \quad (XIII)$$

[7] Busch, *Ber.*, **29**, 2114 (1896).

[8] Mignonac, *Compt. rend.*, **172**, 223 (1921).

[9] Skita and Kiel, *Ber.*, **61B**, 1682 (1928).

[10] Manske and Johnson, THIS JOURNAL, **51**, 580 (1929).

This method has proved to be very satisfactory in this Laboratory in the preparation over a nickel catalyst of cyclohexyl-*n*-butylamine, *n*-butyl-β-phenylethylamine, dicyclohexylamine and N-*n*-butylpiperidine.

## Experimental Results

The nickel catalysts were prepared and used as previously described.[1] Unless stated otherwise the reactions were carried out at 200° under a pressure of approximately 100 atmospheres of hydrogen.

There are listed in Table I for certain alkylation experiments the names and amounts in moles of reactants, the time of heating, the weight of catalyst, the weights and boiling ranges of the more important fractions and such information or modification of the procedure and identification and analysis of products as is necessary.

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS IN SIMPLE ALKYLATIONS

| Amines | Moles | Alcohol | Moles | Time, hrs. | Catalyst, g. | Products |
|---|---|---|---|---|---|---|
| Cyclohexylamine | 0.55 | Ethanol | 1.2 | 4.5 | 4 | Cyclohexylamine 8.6 g. (130–140°) (16%)<br>N-Ethylcyclohexylamine 31.5 g. (46%) (155–160°)[a]<br>N-Diethylcyclohexylamine 6.0 g. (14%) (190–210°) |
| Piperidine | .5 | Ethanol[b] | 1.0 | 3.5 | 2 | N-Ethylpiperidine 44.5 g. (80%) (125–129°)[c] |
| α-Methylpiperidine | .5 | Ethanol | 1.0 | 7.0 | 3 | N-Ethyl-α-methylpiperidine 53 g. (84%) (145–147°)[d] |
| β-Phenylethylamine | .33 | Butanol-1[b] | 0.68 | 4 | 4 | β-Phenylethylamine 17 g. (78–85°) (10 mm.) (43%)<br>N-*n*-Butylphenylethylamine 20 g. (125–130°) (10 mm.) (34%)<br>N-Di-*n*-butylphenylethylamine 10 g. (160–170°) (10 mm.) (13%)<br>Di-β-phenylethylamine 6.2 g. (195–205°) (10 mm.) (9%) |
| α-Methylpiperidine | .5 | Butanol-1[b] | 1.0 | 3.5 | 3 | N-*n*-Butyl-α-methylpiperidine 60 g. (78%) (185–190°)[e] |
| Piperidine | .5 | Ethanol | 1.0 | 3.5 | 2 | N-Ethylpiperidine 42.7 g. (78%) (125–129°)[c] |
| Piperidine | .45 | Butanol-1 | 0.5 | 3.5 | 3 | N-*n*-Butylpiperidine 22.1 g. (35%) (167–172°)[f] |
| *n*-Amylamine | .5 | Butanol-1 (or ethanol) | 1.0 | 3.5 | 3 | *n*-Amylamine 20.2 g. (100–105°) (47%)<br>Di-*n*-amylamine 12 g. (200–205°) (36%) |
| Piperidine | .45 | Cyclohexanol | 0.9 | 7.8 | 4 | N-Cyclohexylpiperidine 57 g. (76%) (98–100°) (10 mm.)[g] |
| α-Methylpiperidine | .21 | Ethanol | 0.5 | 3 | 1 | N-Ethyl-α-methylpiperidine 16 g. (145–147°) (60%) |
| *n*-Amylamine | .29 | None | ... | 3.5 | 1 | Ammonia and di-*n*-amylamine |
| Cyclohexylamine | .25 | None | ... | 3.5 | 1 | Cyclohexylamine 15 g. (130–134°) (60%)<br>Dicyclohexylamine 8 g. (245–253°) (36%) |

[a] The m. p. of the phenylisocyanate derivative 124–125°; *cf.* Sabatier and Senderens.

*Compt. rend.*, **138**, 457, 1257 (1904). [b] The alkylation was made under nitrogen. [c] The m. p. of picrate 165–166°; *cf.* Evans, *J. Chem. Soc.*, **71**, 522 (1897). [d] The m. p. of the picrate from alcohol 188–189°; *cf.* Ladenburg, *Ann.*, **304**, 56 (1899). [e] M. p. of picrate 113–114°. The hydrochloride was prepared in ether solution. *Anal.* Calcd. for $C_{10}H_{22}NCl$: Cl, 18.54. Found: Cl, 18.61. [f] The low yield was due to the smaller amount of alcohol. M. p. of the picrate of the secondary amine 132°. *Cf.* von Braun, *Ber.*, **40**, 3930 (1908). [g] M. p. of picrate 127–127.5°. Hydrochloride. *Anal.* Calcd. for $C_{11}H_{22}NCl$: Cl, 17.45. Found: Cl, 17.48.

There are summarized in Table II the more significant data in the hydrogenation of various compounds.

TABLE II

HYDROGENATION OF VARIOUS COMPOUNDS

| Hydrogen acceptor | Moles | Temp., °C. | Time, hours | Catalyst, g. | Products |
|---|---|---|---|---|---|
| Benzyl cyanide | 1.0 | 125 | 2 | 5 | β-Phenylethylamine 90 g. (74%)<br>Di-β-phenylethylamine 28 g. (25%) |
| Butyl cyanide | 0.96 | 150 | 2 | 5 | *n*-Amylamine 50 g. (100–105°) (60%)<br>Di-*n*-amylamine 14.5 (200–208°) (20%) |
| Butyl cyanide (50 cc. ether) | .5 | 125 | 2.5 | 2 | *n*-Amylamine 25.1 g. (56%) (102–106°)<br>Di-*n*-amylamine 8.8 (22%) (200–208°) |
| Butyl cyanide (60 cc. ethanol) | .5 | 150 | 4 | 3 | *n*-Amylamine 14.5 g. (32.5%) (102–106°)[a]<br>Di-*n*-amylamine 8.9 (22.3%) (200–208°) |
| Benzyl cyanide (50 cc. β-phenylethylamine | .6 | 125 | 1.7 | 3 | β-Phenylethylamine (solvent and product)<br>Di-β-phenylethylamine (0.07 mole) (23%) |
| Hydrobenzamide (in 110 cc. of ethanol) | .16 | 100 | 0.6 | 4 | Benzylamine 16.8 g. (60–64°) (4 mm.) (94%)[b]<br>Di-benzylamine 31.8 (120–123°) (1 mm.) (96%) |
| Benzalaniline (in 50 cc. of ethanol) | .077 | 70 | 0.25 | 1 | Benzylaniline 13.5 g. (96.5%) (144–146°) (1 mm.) |
| α-Benzaldoxime (in 80 cc. of ethanol) | .33 | 100 | 0.75 | 3 | Benzylamine 27.2 g. (77%) (47–50°) (1 mm.)<br>Dibenzylamine 6.2 g. (19%) (160–164°) (1 mm.) |
| α,β-Cinnamaldoxime (in 70 cc. ether) | .33 | 100 | 2 | 3 | γ-Phenylpropylamine 20.8 g. (75–80°) (1 mm.) (42%) |
| Sodium *p*-dimethylaminoazobenzene sulfonate in 100 cc. of water | .185 | 100 | 1 | 4 | *p*-Aminodimethylaniline 17.6 g. (87%) (95–100°) (1 mm.)<br>*p*-Sulfanilic acid 23 g. (72%) |
| (Cyclohexylamine) | .4 | 125 | 2 | 4 | Cyclohexanol 11.2 g. (155–165°) (28%) |
| (Cyclohexanone) | .4 | | | | Dicyclohexylamine 50.3 g. (70%) (115–120°) (10 mm.)[c] |
| Cyclohexylamine | .5 | 125 | 1 | 4 | N-*n*-Butylcyclohexylamine 70.1 g. (200–204°) (91%)[d] |
| Butyraldehyde | .55 | | | | |
| Piperidine | .45 | 125 | 2 | 4 | N-*n*-butylpiperidine 55 g. (93%) (170–174°)[e] |
| Butyraldehyde | .5 | | | | |
| β-Phenylethylamine | .41 | 125 | 1 | 4 | β-Phenylethylamine 10.3 g. 80–85° (10 mm.) (21%)<br>N-*n*-Butyl-β-phenylethylamine 26.2 g., 130–135° (10 mm.)[f] (36%)<br>N-Di-*n*-butyl-β-phenylethylamine 10 g. 162–168° (10 mm.)[g] (11%) |
| Butyraldehyde | .42 | | | | |

[a] The low yield is due to the loss of amine in the distillation of the alcohol. [b] M. p. of benzoyl derivative 106°. [c] M. p. of hydrochloride 333°. *Anal.* Calcd. for $C_{12}H_{24}$-

NCl: Cl, 16.29. Found: Cl, 16.16. [d] Hydrochloride. *Anal.* Calcd. for $C_{10}H_{22}NCl$: Cl, 18.53. Found: Cl, 18.41. [e] M. p. of picrate 131–132°; *cf.* v. Braun, *Ber.*, **40**, 3930 (1908). [f] Hydrochloride. *Anal.* Calcd. for $C_{12}H_{20}NCl$: Cl, 16.61. Found: Cl, 16.72. [g] Hydrochloride, *Anal.* Calcd. for $C_{16}H_{28}NCl$: Cl, 13.18. Found: Cl, 13.01.

## Summary

The formation of secondary amines from primary amines or during the hydrogenation of cyanides, oximes, etc., over a nickel catalyst may result from three types of reactions: (1) reaction of amines with alcohol with the elimination of water; (2) reaction of two molecules of an amine with elimination of ammonia; (3) reaction of alkylidene imines with themselves or with amines. Reactions of types 1 and 2 are induced by the nickel catalyst used in this Laboratory at temperatures above 160–170°. These reactions account in whole or in part for the secondary amines formed in hydrogenations carried out above this range of temperature. Reactions of type 3 do not require a catalyst and occur spontaneously at room temperature. Reactions of this type account for the formation of secondary amines in the hydrogenation of cyanides and oximes and probably of other nitrogenous compounds which can be hydrogenated below approximately 175°. The amount of material entering into these three types of "side" reactions may be minimized by the use of more active nickel catalysts.

The following transformations have been carried out sufficiently successfully with a nickel catalyst so that the methods used seem to merit consideration for preparing these and similar compounds: N-ethylcyclohexylamine from ethanol and cyclohexylamine, N-ethylpiperidine from ethanol and piperidine, N-ethyl-α-methylpiperidine from ethanol and α-methylpiperidine, N-butyl-β-phenylethylamine from butanol and β-phenylethylamine, N-butyl-α-methylpiperidine from butanol and α-methylpiperidine, N-cyclohexylpiperidine from cyclohexanol and piperidine, N-butylpiperidine from butyraldehyde and piperidine, dicyclohexylamine from cyclohexylamine and cyclohexanone, N-butylcyclohexylamine from butyraldehyde and cyclohexylamine, N-*n*-butyl-β-phenylethylamine from butyraldehyde and β-phenylethylamine, diamyl and dicyclohexylamine from the corresponding primary amines, *n*-amyl and di-*n*-amylamine from butyl cyanide, benzyl and dibenzylamines from hydrobenzamide, *p*-aminodimethylaniline from methyl orange, benzylamine from benzaldoxime and γ-phenylpropylamine from cinnamaldoxime.

MADISON, WISCONSIN

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

# DIHYDRO-1,4-PYRANS. II. DEGRADATION BY USE OF THE BECKMANN REARRANGEMENT

BY TSI YU KAO AND REYNOLD C. FUSON

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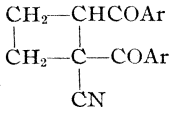
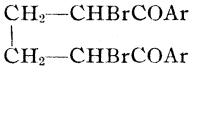
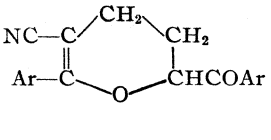
It has been reported[1] that when 1,4-dibromo-1,4-diaroylbutanes (I) are treated with sodium cyanide in a mixture of absolute alcohol and ethyl acetate they do not yield the 1-cyano-1,2-diaroylcyclobutanes (II) to be expected by analogy with the results obtained when this method was applied to $\alpha,\alpha'$-dibromo-adipic esters.[2] Instead, they are transformed into dihydro-1,4-pyrans of the type 2-aryl-3-cyano-6-aroyl-5,6-dihydro-1,4-pyran (III).



II



I



III

Actually, the two compounds (of types II and III) are in each case unknown, and the properties of those actually obtained are such as to make it difficult to decide which type of formula should be assigned to them.

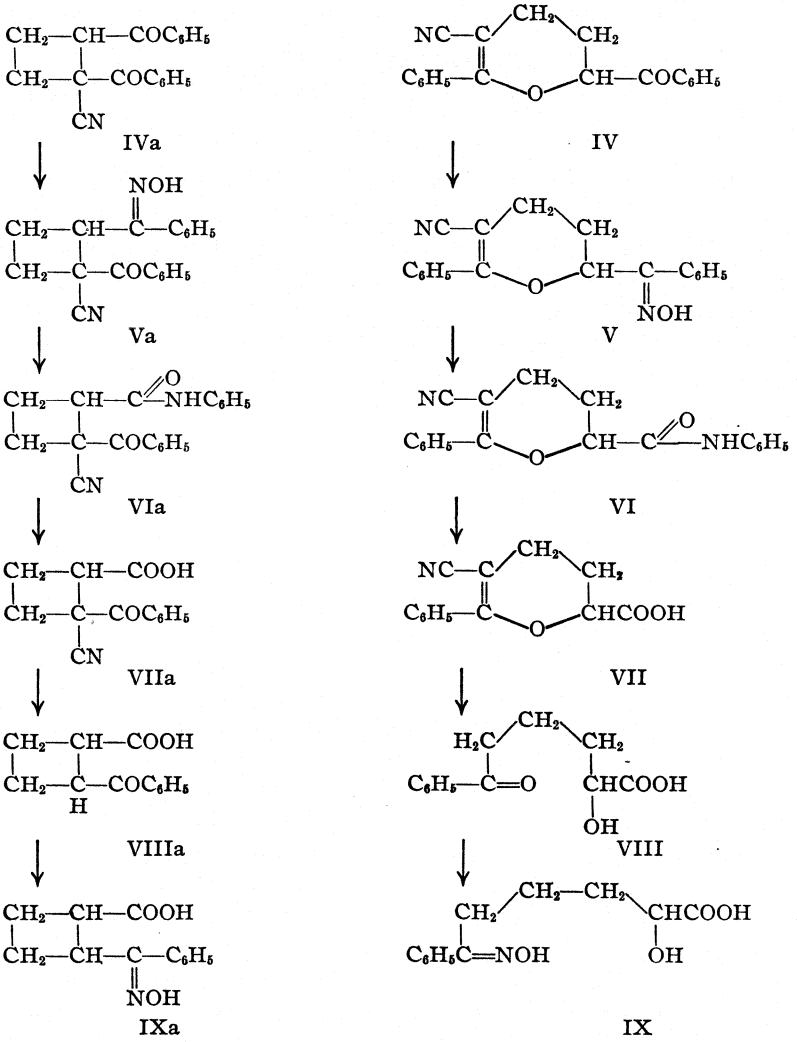
The present paper is a report of a study of this question. For this work the product obtained from 1,4-dibromo-1,4-dibenzoylbutane has been chosen. It should be either 1-cyano-1,2-dibenzoylcyclobutane (IVa) or 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran (IV).

In view of the close similarity between this case and that of the $\alpha,\alpha'$-dibromo-adipic ester cyclization to cyclobutane derivatives, it seemed likely that formula IVa would be found to be correct. Accordingly, in order to form a plan of attack on the problem of structure, this formula was assumed. The plan devised was to prepare the dioxime and by means of the Beckmann rearrangement, followed by hydrolysis and loss of carbon dioxide, to arrive at cyclobutane-1,2-dicarboxylic acid—a known compound.

The attempt to carry out this plan led to the preparation of a series of compounds corresponding rather closely to those to be expected on the basis of the original assumption. However, certain developments, to be mentioned presently, pointed to the 1,4-pyran type of structure (IV) and the problem resolved itself into an attempt to discover unequivocal evidence in favor of one or the other of the two proposed structures. Since

[1] Fuson, Kuykendall and Wilhelm, THIS JOURNAL, **53**, 4187 (1931).

[2] Fuson and Kao, *ibid.*, **51**, 1536 (1929); Fuson, Kreimeier and Nimmo, *ibid.*, **52**, 4074 (1930).




the weight of evidence now at hand is strongly in favor of formula IV, it will be convenient to assume this structure in order to expedite the presentation of the facts upon which the decision rests.

In the first place, the original cyano compound (IV) was a colorless solid melting at 105–106°. Under no conditions has it been found possible to open the ring. It did not decolorize an acetone solution of alkaline permanganate and took up bromine very slowly to form an unstable derivative which appeared to be a monobromo derivative. The original cyano compound formed a monoxime and a monosemicarbazone but under no circumstances could any evidence be obtained of the presence of a second ketone

group. This was the first evidence which strongly favored the monoketone structure (IV) as compared with the diketone structure (IVa).

The monoxime was found to exist in two forms melting at 156.6–157° and 141–142°. However, when treated with thionyl chloride both oximes gave the anilide VI—a compound melting at 156–156.5°. When hydrolyzed, the anilide gave the corresponding acid (VII), melting at 155–156°. This acid did not form an oxime—a fact which militates in favor of formula VII as compared with VIIa since the latter does have a ketone group.

By careful hydrolysis in alkaline solution the cyano acid was converted into the corresponding dicarboxylic acid. This acid gave the calculated neutral equivalent but its instability prevented a satisfactory analysis being made. When this acid was treated with hydrochloric acid it lost carbon dioxide and gave a ketonic acid whose analysis corresponded to formula VII (=VIIIa + $H_2O$). The monoxime of this acid corresponded to formula IX (=IXa + $H_2O$).

It would seem certain that formulas VIIIa and IXa would have to be discarded in favor of VIII and IX, respectively. To settle this point definitely an independent synthesis of δ-benzoyl-α-hydroxyvaleric acid (VIII) has been carried out. This compound, whose preparation will be described elsewhere, has been found to be identical with the degradation product obtained from VII.

It is evident, in the light of this result, that the ring must have opened in the transformation of VII into VIII. This is easily explained by reference to formula VII and seems to exclude the cyclobutane type of structure (VIIa) as a possibility. Also, there is every reason to believe that compounds IV, V and VI are of the same type as VII, an assumption which leads to the conclusion that the formula III (and not formula II) correctly represents the cyclization products obtained by the cyanide treatment of the 1,4-dibromo-1,4-diaroylbutanes.

## Experimental Part

**2-Phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran (IV).**—This compound was prepared from 1,4-dibromo-1,4-dibenzoylbutane by the method of Fuson, Kuykendall and Wilhelm.[1] The yields were about 50% of the theoretical. The closure evidently is accompanied by side reactions. A sticky red liquid was always obtained as by-product and from this has been isolated a bromine-containing compound melting at 138–139°. This compound is under investigation.

**Mono-oximes.**—Two and nine-tenths grams of 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran was dissolved in a mixture of 30 cc. of ethyl alcohol and 10 cc. of water. To this solution were added 3 g. of hydroxylamine hydrochloride and 6 g. of potassium acetate in 15 cc. of water. The mixture was heated on a steam-bath for thirty minutes under a reflux condenser. The reaction mixture was stirred continuously throughout the period of heating and then for an hour or two longer. When allowed to stand at room temperature for twelve hours, the solution deposited crystals melting at 130 to 155°. The mother liquor after the crystals had been removed by filtration was then diluted with water; a precipitate was obtained which set to a gummy mass. Both

this and the first crop of crystals were repeatedly recrystallized from 70% alcohol. In this way two compounds were obtained melting at 156.5–157° (A) and 141–142° (B). In the separation of these compounds much difficulty was encountered; it was comparatively easy in those runs in which the crude product melted above 145° to separate the high-melting compound (A) but in other runs the separation was very difficult and was not always accomplished. Fortunately, as will be seen in the sequel, the separation proved to be unnecessary for the purpose in view. That the two compounds were mono-oximes was shown by the analyses.

*Anal.* Calcd. for $C_{19}H_{16}O_2N_2$: C, 75.0; H, 5.3; N, 9.2. Found for Compound A: C, 75.0; H, 5.3; N, 9.6. Found for Compound B: C, 74.8; H, 5.4.

**The Anilide of 2-Phenyl-3-cyano-6-carboxy-5,6-dihydro-1,4-pyran (VI).**—Both of the mono-oximes (A and B) were subjected to the Beckmann rearrangement. One gram of the dry oxime was added in small portions to a mixture of 3 cc. of thionyl chloride and 7 cc. of chloroform contained in a 50-cc. Erlenmeyer flask surrounded by an ice-bath. After the addition was completed the reaction mixture was allowed to stand for a few minutes in the ice-bath and then for about an hour at room temperature. The temperature gradually rose to 30° and the color of the mixture changed from a light yellow to a pink or faint purple.

The excess thionyl chloride was decomposed by adding cracked ice to the reaction mixture. After the evolution of sulfur dioxide had ceased, 20 cc. of chloroform was added and the chloroform layer was separated and washed twice with water. After the chloroform solution had been dried over anhydrous magnesium sulfate, the chloroform was evaporated under diminished pressure. The residue set to a colorless solid which was washed on a filter with a little cold alcohol and then recrystallized three times from 95% alcohol.

The anilides obtained by the above procedure from the two mono-oximes proved to be identical. The melting point was 156–156.5°; a mixture of the two samples showed no depression of the melting point. Mixtures of the anilide with the original oximes showed a marked depression of the melting point.

*Anal.* Calcd. for $C_{19}H_{16}O_2N$: C, 75.0; H, 5.3; N, 9.2. Found: C, 75.3; H, 5.6; N, 9.5.

**2-Phenyl-3-cyano-6-carboxy-5,6-dihydro-1,4-pyran (VII).**—Two grams of the anilide was heated under a reflux condenser with 40 cc. of a solution of alcoholic potassium hydroxide (1 part potassium hydroxide, 1 part water and 8 parts alcohol) for thirty minutes and allowed to stand for a few hours at room temperature. The reaction mixture was diluted with two or three times its volume of water and concentrated somewhat by evaporation under diminished pressure to remove the alcohol. The aqueous solution remaining was then cooled to 0° and treated with an excess of dilute hydrochloric acid to precipitate the cyano acid. This compound after a few recrystallizations from 50% alcohol separated in the form of yellowish cubical crystals melting at 155–155.5°. It was soluble in dilute alkalies.

*Anal.* Calcd. for $C_{13}H_{11}O_3N$: C, 68.1; H, 4.8; N, 6.1. Found: C, 68.0; H, 5.1; N, 6.4.

**2-Phenyl-3,6-dicarboxy-5,6-dihydro-1,4-pyran.**—One-half gram of the cyano acid (VII) was heated under a return condenser with a 20% solution of sodium hydroxide. The evolution of ammonia was noticeable after a half hour and continued for twenty hours. When ammonia ceased to be evolved, the heating was discontinued and the reaction mixture, after being cooled to 0°, was acidified with dilute hydrochloric acid. The precipitated silicic acid was removed by filtration and the filtrate, after being saturated with sodium sulfate, was extracted repeatedly with ether. The ether extract

was dried over anhydrous sodium sulfate and evaporated under diminished pressure. There was obtained a residue which, when recrystallized from hot water, separated as colorless crystals melting at 144–144.5°, with evolution of gas. The neutral equivalent was found to be 123; that calculated for 2-phenyl-3,6-dicarboxy-5,6-dihydro-1,4-pyran is 124.

When the hot alkaline reaction mixture was acidified with hydrochloric acid the product obtained was the mono-carboxylic acid (see below).

**δ-Benzoyl-α-hydroxyvaleric Acid (VIII).**—One gram of the cyano acid (VII) was heated under a reflux condenser with 60 cc. of a 50% solution of sulfuric acid. After fifteen minutes of boiling the cyano acid was completely dissolved. The solution darkened rapidly and at the end of an hour dark crystals began to separate. The heating was then discontinued and the reaction mixture was diluted with an equal volume of water. This solution was cooled to 0° and allowed to stand for several hours. The crystals obtained in this way were removed by filtration and recrystallized first from hot water and then from ethyl acetate. The δ-benzoyl-α-hydroxyvaleric acid thus obtained was shown to be identical with that prepared from the dicarboxylic acid as indicated in the preceding section. It melted at 120–120.5°; the yield was 88% of the theoretical.

*Anal.* Calcd. for $C_{12}H_{14}O_4$: C, 64.2; H, 6.3. Found: C, 64.3; H, 6.0.

**Oxime.**—The oxime was a colorless crystalline compound, melting at 144–145.5°; the yield was 63% of the theoretical.

*Anal.* Calcd. for $C_{12}H_{15}O_4N$: C, 60.8; H, 6.4. Found: C, 60.7; H, 6.4.

## Summary

Evidence has been presented in support of a dihydro-1,4-pyran structure for the cyano ketone obtained by the cyanide ring-closure of 1,4-dibromo-1,4-dibenzoylbutane. The anilide obtained by rearrangement of the oxime of the cyano ketone has been found to hydrolyze to δ-benzoyl-α-hydroxyvaleric acid. This result furnishes convincing evidence that the cyano compound is 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# PENTOSE REACTIONS. I. FURFURAL FORMATION

BY CHARLES D. HURD AND LLOYD L. ISENHOUR[1]

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It is generally known that pentoses yield furfural on distillation with mineral acids. This is the basis for the determination[2] of pentoses. Furthermore, the commercial production of furfural[3] depends on the pentosan content of oat hulls. In proportion to the general familiarity with the reaction, detailed study on it has been quite limited.

To ascertain whether or not the reaction of pentose into furfural was merely one of dehydration, xylose was heated with phosphorus pentoxide

[1] Quaker Oats Fellow at Northwestern University, 1927–1929.

[2] Pervier and Gortner, *Ind. Eng. Chem.*, **15**, 1167, 1255 (1923).

[3] Miner and Brownlee, British Patent, 203,691, Dec. 4, 1924; *Chem. Abstracts*, **18**, 692 (1924).

and with zinc chloride (145°). Negligible yields resulted; nor did distillation of xylose with 4 molar phosphoric acid give rise to any furfural.[4] A low yield was formed, however, when xylose was distilled in the presence of a solution of zinc chloride. Distillation of xylose with several salt solutions gave immeasurable quantities of furfural. Solutions such as these were tried: saturated sodium chloride, saturated sodium sulfate, 4.1 molar calcium chloride. The use of 4 molar ammonium sulfate solution gave slight yields.

**Xylose and Mineral Acids.**—Pervier and Gortner[2] demonstrated that steam distillation of the mixture of pentoses and mineral acids increases the yield of furfural, but little attention has been paid to the effect caused by varying the concentration of acids. For a given acid, the important variables are the concentration, the temperature and the duration of the distillation. Almost no furfural was detectable with 3.8 *N* sulfuric acid ($H_2SO_4$, 16% by wt.) at 67°, and only a 2% yield was realized in one and one-half hours at 85°. This yield changed to 38%, however, when a temperature of 107° was taken.

In the technical manufacture of furfural, the yield is dependent on the high temperature which is employed. Five per cent. sulfuric acid is used[5] on the xylan of oat hulls. It is apparent that the yield of furfural at 100–102°, the distillation temperature of the acid at atmospheric pressure, would be nil. However, operating conditions are at a higher temperature (about 145–148°), since a steam pressure of 60 lb./sq. in. is maintained.

Most of the present work was performed at atmospheric pressure with varying concentrations of hydrochloric and sulfuric acids. Hydrochloric acid solutions varied between 1.3 and 5.2 normal (4.7–18.8%), and sulfuric acid concentrations between 3.8 and 12.1 normal (16–52%). Furfural yields were small at the low concentrations but they became higher as the concentration increased. The data are summarized in Tables I and II of the experimental part.

The change of xylose into furfural followed the unimolecular law. By plotting time against log $(a - x)$, the straight line functions shown in Fig. 1 result. This is in keeping with the unimolecular equation

$$k = \frac{2.3}{t} \log \frac{a}{(a - x)}$$

wherein $(a - x)$ represents the quantity of undecomposed xylose at the end of time $t$. From the curves it is evident that sulfuric and hydrochloric

[4] Fukai, *Bul. Ferm.*, **100**, 106 (1928); *Chem. Abstracts*, **23**, 1081 (1929), states that the phosphoric acid distillate of various sugars shows only a faint test for furfurals. For further evidence of furfural formation under conditions where a simple dehydration reaction is unthinkable, see Aronovsky and Gortner, *Ind. Eng. Chem.*, **22**, 264 (1930).

[5] Miner, Trickey and Brownlee, *Chem. Met. Eng.*, **27**, 299, 362 (1922); Killeffer, *Ind. Eng. Chem.*, **18**, 1217 (1926).

acids give similar effects if the normality of the former is about double that of the latter. As the value of $t$ increases, the furfural yield shows a tendency to fall off. This effect is the most pronounced with sulfuric acid in its higher concentrations, as Fig. 1 reveals, where the straight line functions become curved. By extending the hydrochloric acid curves, a similar falling-off would be apparent. This may be taken as evidence that some of the furfural remains in contact with the hot acid long enough to resinify. With the more concentrated acids, the rate of furfural formation may be greater than its rate of removal.

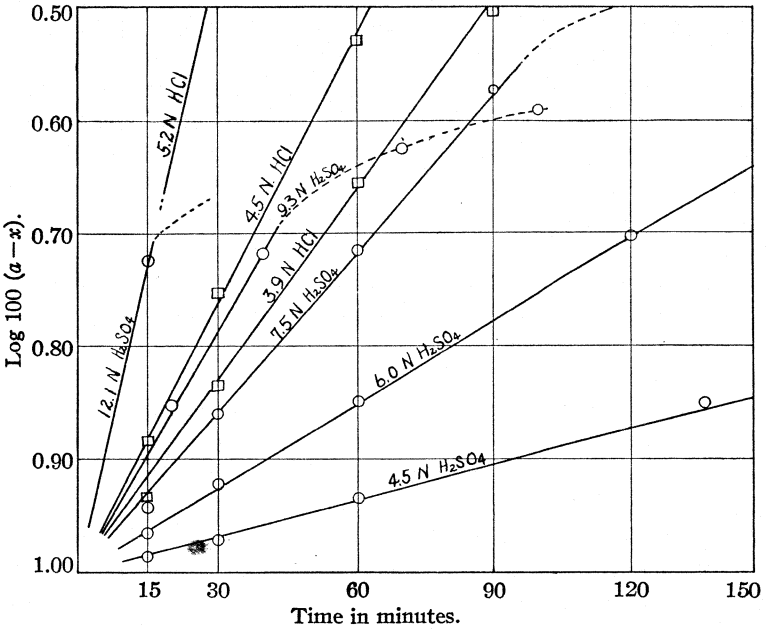



Fig. 1.—Xylose and mineral acids.

An analogous study with rhamnose substantiated this viewpoint. Methylfurfural is formed by distillation with acids, but it does not steam-distil so readily as furfural. When 0.1 g. of rhamnose was steam-distilled with 32% sulfuric acid, a fairly high yield was obtained provided that a large volume of steam was passed through the mixture. With larger quantities of rhamnose or with slower distillation conditions, humin bodies resulted and the yield of methylfurfural was low because of its reaction with the acid.

The higher the concentration of acid, the higher was its distillation temperature. A range from 101 to 107° was encountered in hydrochloric acid, and 103 to 127° with sulfuric acid. As was demonstrated above, the increased boiling temperature of the more concentrated solutions plays a

part in furfural production, but two other factors enter. First, is the hydrogen-ion concentration and, second, is the nature of the acid. Nitric acid (19% concentration), for example, gave only 1.5% yield of furfural after thirty minutes of steam distillation. Trichloroacetic acid (4 molar) was no better.

Thinking that "superacid" solutions[6] might sponsor furfural production from xylose, this substance was placed in a dilute solution of sulfuric acid in butyric acid and the mixture distilled. Only a 3% yield of furfural was realized in two and one-half hours. A negligible yield came also when a mixture of xylose, acetic acid and benzenesulfonic acid was distilled.

**Humins from Furfural.**—The reaction of furfural with acids, according to Marcusson,[7] leads to humins and humic acid. In studying this reaction further, it was learned that refluxing furfural for two hours in hydrochloric acid of 18.8% strength destroyed three-fifths of the furfural. If such a solution was steam-distilled instead of refluxed, 99.5% recovery of the furfural was attainable.

Both alkali-soluble humic acid and alkali-insoluble humin were formed when furfural was slowly added to a refluxing solution of 14% hydrochloric acid. At the end of three hours, all but one-fourth of the furfural had entered into reaction, the reaction product being a black precipitate. The carbon content of this substance was determined by sodium peroxide fusion[8] and also by a chromic acid oxidation method.[9] A difference of 13% between the two determinations, the former giving the higher value, points to the presence of some free carbon or else to the presence of polymeric humins of such complexity that their oxidation by the chromic acid method is a matter of difficulty.

**Other Pentoses and Mineral Acids.**—Steam distillation of arabinose from 32% sulfuric acid gave a 45% yield of furfural. Under identical conditions, the yield from xylose was 70% of the calculated. Possibly there is a relationship between these values and the velocity coefficients of mutarotation ($k$) of the pentoses.[10] At least, it seems reasonable to believe that the initial effect of acid on a sugar is to convert it from the cyclic "hemi-acetal" form into the "aldehyde" form. The values of $k$ for xylose and arabinose, respectively, are 0.021 and 0.031. The quotient of $1.5/k$ equals 74 and 45, values which are surprisingly close to the yields of furfural with the same sugars. With $k$ for lyxose given as 0.065, then $1.5/k$ is 22. It may be predicted that the yield of furfural from lyxose (with 32%

[6] Conant and Hall, THIS JOURNAL, **49**, 3062 (1927).

[7] Gortner, *J. Biol. Chem.*, **26**, 194 (1916); Marcusson, *Ber.*, **54**, 542 (1921).

[8] Parr, "The Analysis of Fuel, Gas, Water and Lubricants," McGraw-Hill Book Co., New York, **1912**, p. 179.

[9] Florentine, *Bull. soc. chim.*, **31**, 1068 (1922); **35**, 228 (1924).

[10] Hudson, "Relations between Rotatory Power and Structure in the Sugar Group," Sci. Papers of the Bureau of Standards, No. 553, U. S. Printing Office, 1926, p. 271.

sulfuric acid) would be less than from arabinose. It would be interesting to learn if the yield were in the vicinity of 22%.

Experiments with rhamnose indicated it to be of the same order of activity as arabinose for furfural production, but the distillation rate for methylfurfural so differs from the rate for furfural that the results may not be strictly comparable.

It was of interest to study the behavior of ketoxylose, $CH_2OH(CHOH)_2COCH_2OH$, with acids. We are indebted to C. E. Gross[11] of this Laboratory who furnished us with a polymeric modification of this ketose. Its molecular weight indicated that it was a tetrasaccharide, $(4C_5H_{10}O_5-3H_2O)$. This ketose was distilled with 32% sulfuric acid. During the first half hour, slightly less than a 5% yield of furfural was formed, but no more came by prolonging the distillation. Figure 2 shows graphically the rate of furfural production of the various pentoses which have been considered.

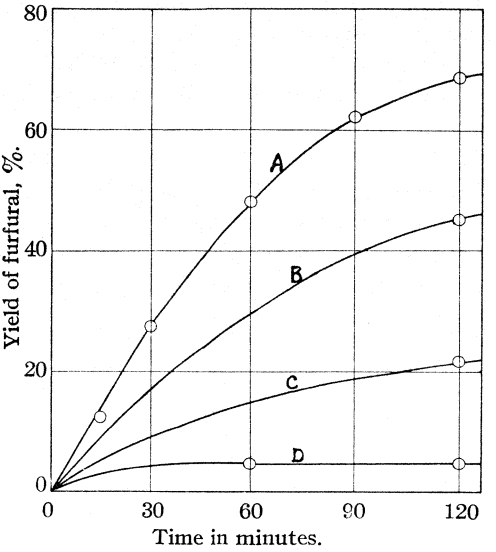
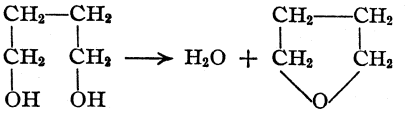



Fig. 2.—Furfural from various pentoses with 7.5 *N* sulfuric acid: A, xylose; B, arabinose; C, predicted curve for lyxose; D, ketoxylose polymer.

**Tetrahydrofuran.**—Tetramethylene glycol was prepared by reduction of diethyl succinate. When this glycol was refluxed with 7.5 *N* sulfuric acid (32%), a 76% yield of tetrahydrofuran was realized



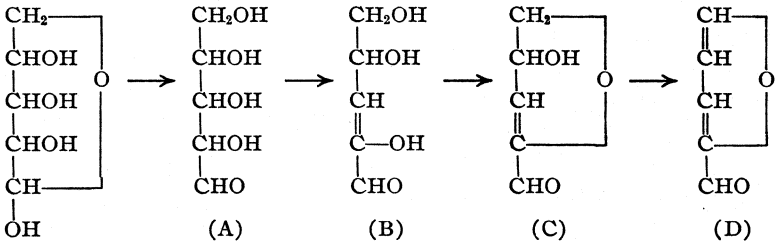

It was thought that erythritol should also give rise to a furan ring closure on heating with acids. However, no change at all was observed when mesoerythritol was refluxed for six and one-half hours with 7.5 *N* sulfuric acid. The fact that tetramethylene glycol yields tetrahydrofuran more easily than xylose yields furfural is difficult to reconcile with this non-formation of furan from natural erythritol. However, just as arabinose and xylose differ in their ease of furfural formation, so it is possible that *d*-, *l*- or *dl*-erythritol would behave differently from mesoerythritol in this respect.

[11] Gross and Lewis, THIS JOURNAL, **53**, 2777 (1931).

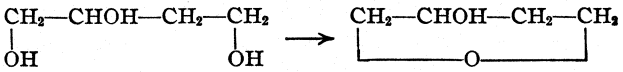
Attempts to synthesize *d*-erythritol were unsatisfactory, so we have no information on this point.

The cadmium xylonate-cadmium bromide double salt was refluxed for two hours in 3.9 *N* hydrochloric acid. No furoic acid could be detected as a reaction product.

**Mechanism of Furfural Formation.**—Whether or not an aldopentose is considered to possess the cyclic hemi-acetal formula or the open-chain aldehyde formula, it seems obvious that the latter is an essential intermediate between the former and furfural. Acetals, quite generally, are hydrolyzed by acids. Following Fittig's suggestion,[12] it has often been assumed that dehydration into a heterocyclic ring is the first step. In our opinion, this is the second step, the first one being a dehydration to an $\alpha,\beta$-unsaturated aldehyde as follows

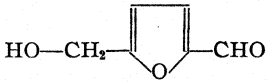



These facts support such a picture. (1) $\beta$-Hydroxyaldehydes, such as aldol, lose water very readily in the manner of (A) to (B). (2) Secondary alcohols which are not $\beta$-hydroxyaldehydes also lose water in the manner of (A) to (B), but much less readily. Just as isopropyl alcohol is more difficult to dehydrate to an unsaturated compound than aldol (compare $[CH_3CHOH—CH_2]H$ and $[CH_3CHOH—CH_2]CHO$), so erythritol should be more difficult to dehydrate to an unsaturated compound than an aldopentose (compare [R—CHOH—CHOH]H and [R—CHOH—CHOH]-CHO, wherein R is the radical $CH_2OH—CHOH—$). Actually, furan could not be formed from erythritol. This suggests that step (C) cannot be realized in the case of erythritol, because the change from (A) to (B) is blocked. (3) The formation of tetrahydrofuran from tetramethylene glycol demonstrates how readily a furan ring closure may be effected when no interfering hydroxyl groups are present. Several other cases of furan ring closure from the action of acids on gamma glycols are listed in the literature. The fact that butanetriol-1,2,4 may be converted into hydroxytetrahydrofuran

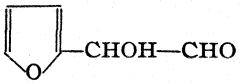


[12] Fittig, *Ann.*, **303**, 169 (1898).

on boiling with water[13] shows that the presence of one hydroxyl group on the chain does not exert steric hindrance to prevent ring closure. (4) Unless step (B) precedes step (C), it is difficult to explain why the cause which blocks erythritol does not also block xylose. (5) Applied to the hexoses, this mechanism leads logically to the production of hydroxymethylfurfural. If the first step were regarded as that of heterocyclic ring



Hydroxymethylfurfural



Furylglycolic aldehyde

formation, both this compound and its isomer furylgylcolic aldehyde should result for ring closure of this type should occur equally readily in a hexose between carbon atoms 2,5, or 3,6. Only the former evidently occurs.

## Experimental Part

Xylose was synthesized from corn cobs[14] hy hydrolysis with dilute sulfuric acid (7%) following the usual method. From 1 kg. of cobs, 100 g. of pure xylose was obtained. For some of the concluding experiments in this work, xylose was generously donated by the Bureau of Standards.

**Xylose from Oat Hulls.**—Except for a preliminary soaking in ammonium hydroxide and for somewhat milder conditions of acid hydrolysis, oat hulls were hydrolyzed to xylose using a method which was similar to that used with corn cobs. Xylose was definitely identified but difficulties in the purification procedure limited the yield to about one-third that from corn cobs.

A mixture of 4 liters of water, 400 cc. of concd. ammonium hydroxide and 500 g. of oat hulls was left at room temperature for fifty-two hours. Then the hulls were filtered off and washed with 4 liters of water. The hulls were placed in 3 liters of water which contained 350 cc. of concd. sulfuric acid. After twenty-three hours, 3 liters of water was added and the mixture was left for seventy-two hours more, following which it was refluxed for one hour. After filtration, the filtrate was almost neutralized with calcium hydroxide and the neutralization completed with calcium carbonate. The calcium sulfate was collected on a filter and washed with 2 liters of water. The filtrate was made acid with 5 cc. of 85% phosphoric acid, 30 g. of decolorizing carbon added, air bubbled through the warm suspension for half an hour and finally filtered. The filtrate was concentrated under diminished pressure to a volume of 400 cc. No darkening occurred. A liter of alcohol was added and the precipitate of calcium sulfate removed. The filtrate from this operation was concentrated to a thick sirup (about 100 cc.) under reduced pressure, cooled and diluted with an equal volume of absolute alcohol. After seeding with a small crystal of xylose, the mixture was left for two weeks in a desiccator over sulfuric acid. The mass was then placed on a suction filter overnight after it had been thinned with about 25 cc. of 90% alcohol. About 40 g. of a mixture of xylose and gum was obtained. This was dissolved in 75 cc. of hot 90% alcohol. The solution was evaporated to a thick sirup on the steam-bath, seeded with a crystal of xylose and crystallized in a desiccator. The crystals which resulted were filtered and washed thoroughly with four 20-cc. portions of 80% alcohol and finally with a little absolute alcohol. The yield of dry crystals was 14 g., or 2.8%.

[13] Pariselle, *Ann. chim. phys.*, **24**, 315 (1911).

[14] Hudson and Harding, THIS JOURNAL, **40**, 1601 (1918); Harding, *Sugar*, **25**, 124 (1923).

**Identification.**—Two grams of the crystalline product was dissolved in 20 cc. of water and the volume made up to 25 cc. The optical rotation was then determined, using a one-decimeter tube. This gave a constant rotation of +1.5°, from which the specific rotation is +18.75°. Hudson's value[15] is 19°. This rotation did not change when the solution was left for two months.

For further identification of the pentose from the oat hulls, the crystals were converted to xylosazone[16] which melted at 156° (corr.) and to the double salt of cadmium bromide and cadmium xylonate. The latter is especially characteristic of xylose.

Beautifully formed crystals of the xylose were obtained by crystallization from 90% alcohol in a desiccator. When examined under a polarizing microscope, the crystals were found to be of the negative biaxial type. The alpha index of refraction was 1.515 and the beta index 1.540. These values agree with the published values of Wherry,[17] namely, 1.517 and 1.544.

**Furfural Analysis.**—The colorimetric method of Youngberg and Pucher[18] using aniline acetate in an excess of acetic acid was employed. For careful work, about forty-five minutes was required from one analysis to the next, but approximate results could be obtained in fifteen minutes. Youngberg and Pucher recommended the use of standard comparison solutions of 0.02 and 0.05 mg. furfural per cc. In the present work, a 0.05-mg. standard has served all purposes. Its use allows the concentration of the unknown to vary from 0.01 to 0.09 mg. per cc. Where the furfural content of the unknown was as low as 0.01 mg. per cc., 4 cc. was matched against 1 cc. of the standard, thus making the ratio of the total furfural contents as 4 to 5. This permitted accurate analysis.

A colorimetric method using benzidine[19] was studied. It cannot be recommended, for the color faded rapidly. In addition, the color was much harder to match than that obtained by the aniline acetate method.

A reagent which was useful in determining the end-point of a furfural steam-distillation was a mixture of 1 cc. of glacial acetic acid and 0.5 cc. of aniline. When 2 to 3 cc. of distillate gave no coloration with this reagent in one minute, furfural was considered to be absent. This was somewhat more satisfactory than the aniline hydrochloride paper which was recommended by Pervier and Gortner.

## Production of Furfural from Xylose

**Phosphorus Pentoxide.**—When 0.5 g. of xylose and 2 g. of phosphoric anhydride were heated in a distilling flask at 107° and 80 mm. for five hours, there was no evidence of a distillate which contained furfural. The aniline acetate test was negative, whereas minute quantities of furfural give a red coloration with aniline in acetic acid.

**Zinc Chloride. (a) Without Water.**—Xylose (0.5 g.) and zinc chloride in excess were heated for twenty-five minutes at 145° and 80 mm. A slight charring occurred and a trace of distillate was collected. It contained about 1.5 mg. of furfural; yield, less than 0.1%.

**(b) With Water. Very Concentrated Solution.**—In a 25-cc. distilling flask were placed 0.36 g. of xylose, 0.25 cc. of water and 1.0 g. of zinc chloride. It was connected to an ice-cooled receiver and the pressure lowered to 45 mm. Heating in a bath at 180° caused vigorous bubbling for ten minutes, after which a charred, porous mass remained. The distillate was diluted to a volume of 350 cc. and analyzed. The furfural content showed a 15.3% yield.

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[15] Hudson, Ref. 10, p. 269.

[16] Heuser and Brunner, *J. prakt. Chem.*, **104,** 279 (1922).

[17] Wherry, THIS JOURNAL, **40,** 1852 (1918).

[18] Youngberg and Pucher, *J. Biol. Chem.*, **61,** 741 (1924).

[19] McCance, *Biochem. J.*, **20,** 1111 (1926).

The data of this analysis will be listed, but not in subsequent analyses. From the 350 cc. of unknown solution, 1 cc. was matched colorimetrically against 2 cc. of a standard which contained 0.10 mg. (0.05 mg. per cc.) of furfural. In most of the analyses, 1 cc. of the unknown was matched against 1 cc. of the standard. The depth of the standard solution was 31 mm., whereas the unknown solution matched it at 30.8 mm. Thus, the 1 cc. of unknown solution contained (31/30.8) (0.10 mg.) or 0.10064 mg. of furfural. From this, the 350 cc. contained 35.225 mg., as opposed to a theoretical yield of 229.5 mg.; percentage yield, 15.3.

**Four Molar Zinc Chloride (4.4 *M*).**—A solution of 0.1 g. of xylose, 120 g. of zinc chloride and water was made up to 200 cc. The solution was steam distilled during two hours. The distillate was collected in four periods, at the end of fifteen, thirty, sixty and one hundred and twenty minutes from the start. Furfural analyses on each gave 2.47, 9.7, 15.9 and 13.11% yields, respectively, or a total yield of 41.2%. The temperature of the reaction mixture rose from 108 to 109.5° during the first thirty minutes. The subsequent temperature was 109.5–110°.

**Other Salts.**—Distillation of xylose from saturated sodium chloride solution, saturated sodium sulfate solution or from a 4.1 molar calcium chloride solution gave nearly immeasurable quantities of furfural. Traces were formed, but only slightly more (due to increased temperature) than would have been formed by distilling xylose from a pure water solution.

## Distillation of Xylose with Acids

**Phosphoric Acid.**—Steam distillation of xylose (0.1 g.) with 4 molar phosphoric acid solution (200 cc. contained 64 g. of $HPO_3$) gave no appreciable quantity of furfural.

**Oxalic Acid.**—A solution of xylose in 200 cc. of 4 molar oxalic acid distilled at a temperature of 103°. In forty-five minutes, less than 3% of the xylose had been converted into furfural.

**Trichloroacetic acid,** in 4 molar solution, gave a quantity of furfural which was insufficient to analyze.

**Nitric Acid.**—One-tenth gram of xylose and 150 cc. of a 19.5% solution of nitric acid (3.4 normal) were steam distilled for seven hours. The distillation temperature was 104°. Colorimetric analyses showed that 11.85 mg. of furfural had distilled over in the 435 cc. of distillate, which represented an 18.5% yield. The yield was about 3% at the end of the first hour, which is indicative of a uniform reaction rate.

**Hydrochloric Acid.**—For all studies of the rate of formation of furfural from xylose, the following apparatus was used. A 300-cc. long-necked, round-bottomed flask was fitted with a steam inlet, a thermometer and a vertical 46-cm. delivery tube leading to a condenser. The long delivery tube served as a fractionating column. In this way it was possible to have a large volume of steam coming out of the reaction mixture without the necessity of having an unduly large amount of distillate. Thus, a more efficient removal of the furfural from the reaction mixture was realized without the disadvantage of having a solution too dilute for analysis after the vapor was condensed.

Hydrochloric acid was studied in four concentrations. The results are collected in Table I. The weight of xylose taken for each distillation was 0.1 g. and the original volume of acid solution for each was 200 cc. In the acids of higher concentration, the distillate was collected in five fractions, each of which was analyzed individually.

**Sulfuric Acid.**—Xylose (0.1 g.) was distilled from sulfuric acid solutions of several different concentrations. Two hundred cc. of the acid was always taken, except with the 6.0 *N* acid, when 150 cc. was used. The results are tabulated in Table II. These results, and also the results obtained with hydrochloric acid, are plotted on Fig. 1. With 7.5 *N* acid, or higher, the reaction mixture darkened somewhat as distillation progressed.

TABLE I

XYLOSE AND HYDROCHLORIC ACID

| Acid concn. % by wt. | Acid concn. Normality | Distn. temp., °C. | Distn. period, minutes | Vol. of distillate, cc. | Furfural yield mg. | Furfural yield % | 100 ($a - x$) | $k_{min.}$ |
|---|---|---|---|---|---|---|---|---|
| 4.70 | 1.3 | 101 | 30 | 103 | 0.39 | 0.62 | 9.938 | 0.00021 |
| 9.45 | 2.6 | 102.5 | 510 | 2250 | 56.61 | 88.4[a] | 1.16 | .0042 |
| 14.15 | 3.9 | 104 | 15 | 250 | 8.62 | 13.5 | 8.65 | .010 |
| | | | 15 | 100 | 11.54 | 18.0 | 6.85 | .013 |
| | | | 30 | 100 | 14.71 | 23.0 | 4.55 | .013 |
| | | | 30 | 100 | 8.77 | 13.7 | 3.18 | .013 |
| | | | 30 | 100 | 4.92 | 7.7 | 2.41 | .012 |
| | | Totals | 120 | | | 75.9 | | |
| 16.5 | 4.5 | 106 | 15 | 250 | 15.24 | 23.81 | 7.619 | .018 |
| | | | 15 | 100 | 13.15 | 20.55 | 5.564 | .018 |
| | | | 30 | 250 | 13.95 | 21.80 | 3.384 | .018 |
| | | | 60 | 180 | 10.92 | 17.05 | 1.679 | .015 |
| | | | 70 | 260 | 0.65 | 1.00 | 1.579 | .010 |
| | | Totals | 190 | | | 84.21 | | |
| 18.8 | 5.2 | 107 | 30 | 250 | 46.05 | 72.0 | 2.80 | .042 |
| | | | 30 | 250 | 9.12 | 15.5 | 1.25 | .035 |
| | | | 30 | 114 | 2.38 | 4.1 | 0.84 | .028 |
| | | | 30 | 106 | 0.62 | 1.0 | .74 | .022 |
| | | | 30 | 100 | nil | ... | | |
| | | Totals | 150 | | | 92.6 | | |

[a] Furfural was still being formed at the end of eight and one-half hours.

TABLE II

XYLOSE AND SULFURIC ACID

| Acid concn. % by wt. | Acid concn. Normality | Distn. temp., °C. | Distn. period, minutes | Vol. of distillate, cc. | Furfural yield mg. | Furfural yield % | 100 ($a - x$) | $k_{min.}$ |
|---|---|---|---|---|---|---|---|---|
| 19.2 | 4.5 | 103 | 15 | 50 | 1.59 | 2.5 | 9.75 | 0.0017 |
| | | | 15 | 50 | 2.43 | 3.8 | 9.37 | .0022 |
| | | | 30 | 100 | 4.73 | 7.4 | 8.63 | .0024 |
| | | | 75 | 325 | 10.16 | 15.9 | 7.03 | .0026 |
| | | Totals | 135 | | | 29.6 | | |
| 25.6 | 6.0 | 106 | 15 | 100 | 4.98 | 7.8 | 9.22 | .0054 |
| | | | 15 | 100 | 5.66 | 8.84 | 8.34 | .0061 |
| | | | 30 | 150 | 8.26 | 12.9 | 7.05 | .0059 |
| | | | 60 | 170 | 12.8 | 20.0 | 5.05 | .0057 |
| | | Totals | 120 | | | 49.5 | | |
| 25.6 | 6.0[a] | 106 | 15 | 150 | 10.05 | 8.2 | 9.18 | .0058 |
| | | | 15 | 150 | 12.1 | 9.4 | 8.24 | .0065 |
| | | | 30 | 200 | 20.14 | 15.7 | 6.67 | .0067 |
| | | | 60 | 200 | 27.0 | 21.1 | 4.56 | .0066 |
| | | Totals | 120 | | | 54.4 | | |

TABLE II (*Concluded*)

| Acid concn. % by wt. | Acid concn. Normality | Distn. temp., °C. | Distn. period, minutes | Vol. of distillate, cc. | Furfural yield mg. | Furfural yield % | 100 ($a - x$) | $k_{min.}$ |
|---|---|---|---|---|---|---|---|---|
| 32 | 7.5 | 108.7 | 15 | 250 | 7.91 | 12.36 | 8.76 | 0.009 |
| | | | 15 | 100 | 9.74 | 15.22 | 7.24 | .011 |
| | | | 30 | 100 | 13.16 | 20.56 | 5.19 | .011 |
| | | | 30 | 100 | 8.99 | 14.05 | 3.78 | .011 |
| | | | 30 | 50 | 4.29 | 6.7 | 3.11 | .010 |
| | | Totals | 120 | | | 68.9 | | |
| 40 | 9.3 | 112–113 | 20 | 250 | 18.85 | 29.4 | 7.06 | .017 |
| | | | 20 | 250 | 12.44 | 19.4 | 5.12 | .017 |
| | | | 30 | 250 | 5.68 | 8.9 | 4.23 | .012 |
| | | | 30 | 50 | 0.83 | 1.3 | 4.10 | .009 |
| | | Totals | 100 | | | 59.0 | | |
| 52 | 12.1 | 127 | 15 | 250 | 30.12 | 47.1 | 5.29 | .042 |
| | | | 15[b] | 250 | 0.9 | 1.4 | 5.15 | ... |
| | | Totals | 30 | | | 48.5 | | |
| 16 | 3.8 | 67[c] | .. | 100 | nil | ... | | |
| | | 85[c] | 90 | | | 1.5–2 | 9.83 | .0002 |
| | | 90[c] | 15 | 22 | 0.36 | 0.56 | 9.94 | .0005 |
| | | | 15 | 19.5 | 0.48 | 0.74 | 9.87 | .0004 |
| | | | 30 | 46 | 1.19 | 1.85 | 9.68 | .0005 |
| | | | 30 | 50 | 1.92 | 3.0 | 9.38 | .0007 |
| | | Totals | 90 | | | 6.15 | | |
| 16 | 3.8 | 107[d] | 15 | 75 | 3.84 | 6.0 | 9.40 | .0042 |
| | | | 15 | 50 | 4.6 | 7.2 | 8.68 | .0047 |
| | | | 30 | 100 | 6.91 | 10.8 | 7.60 | .0046 |
| | | | 30 | 100 | 8.82 | 13.8 | 6.22 | .0053 |
| | | Totals | 90 | | | 37.8 | | |

[a] A duplicate run, wherein 0.2 g. of xylose was taken rather than 0.1 g. [b] Continued distillation gave too little furfural to analyze. [c] Reduced pressure in the distilling system. [d] Increased pressure in the distilling system.

## Furfural and Hydrochloric Acid

**Recovery from 5.2 Normal Acid.**—A solution of 100 mg. of furfural in 150 cc. of 5.2 *N* hydrochloric acid was steam-distilled for four and three-fourths hours. The 800 cc. of distillate was diluted to two liters and analyzed for furfural. The quantity present was 99.5 mg., or only 0.5% non-recovery. Under the conditions of this experiment, xylose was shown to yield 90–93% of furfural.

**Refluxing.**—A solution of 5.2 *N* hydrochloric acid which contained 0.4 mg. of furfural per cc. was prepared and refluxed for two hours. The furfural content was then checked colorimetrically against a similar portion which had not been heated. The furfural contents were in the ratio of 4 to 10, showing that 60% of the furfural had been destroyed.

**Humin Formation.**—Twenty-five grams of furfural was added slowly to a refluxing solution of 3.9 *N* hydrochloric acid. After three hours the mixture was cooled and

filtered. A heavy black precipitate had formed during that time. Upon being washed with water and dried, it weighed 15 g. Analysis of the filtrate from the precipitate showed that 6.6 g. of the furfural had not been destroyed. The 15 g. of precipitate, or humin, had been formed from 18.4 g. of furfural. No gaseous or liquid products could be isolated.

Only traces of the humin could be dissolved in organic solvents. The portion known as humic acid could be dissolved in aqueous alkali. The solution was cherry-red in color. Addition of mineral acids precipitated the humic acid from its solution in alkali. This precipitate was flocculent and brown in color. The humic acid was converted into the insoluble humin by refluxing for six to eight hours with mineral acid or by heating alone. The humin was analyzed for carbon by two different methods, by Parr's sodium peroxide fusion method and by Florentine's[9] chromic acid oxidation method. The latter consisted in refluxing the sample with 10 g. of chromic acid, 10 cc. of water, 1 g. of mercuric sulfate and 25 cc. of concd. sulfuric acid. In both, the liberated carbon dioxide was determined volumetrically.

*Anal.* (Sodium peroxide fusion). Found: C, 79.1, 82.0; (chromic acid), 67.6, 67.5.

**Sulfuric Acid with Other Carbohydrates.**—In Table III are summarized the data showing the action of 7.5 *N* sulfuric acid on arabinose, rhamnose and ketoxylose. With rhamnose, which yielded methylfurfural instead of furfural, a colorimetric method was developed similar to the one which was employed for furfural. Pure methylfurfural (2.5 g.) was dissolved in 500 cc. of toluene-saturated water. Three cc. of this solution was made up to 10 cc., and 1 cc. of it (which contained 1.5 mg. of methylfurfural) was compared with 4 cc. of the unknown. To both colorimetric tubes were added 4 cc. of glacial acetic acid, 0.5 cc. of aniline and water to 10 cc. In the rhamnose distillation experiments some tarring occurred. This indicated that not all of the methylfurfural was being removed.

TABLE III

SULFURIC ACID ON OTHER CARBOHYDRATES

| Substance taken | Weight, g. | Vol. of acid, cc. | Distn. period, min. | Vol. of distillate, cc. | Furfural content, mg. | Furfural yield, % |
|---|---|---|---|---|---|---|
| Arabinose | 0.1338 | 150 | 120 | 310 | 38.75 | 45.0 |
| Arabinose | .1590 | 150 | 120 | 550 | 46.58 | 45.7 |
| Rhamnose | .2603 | 150 | 120 | 310 | 80.3 | 51.0 |
| Rhamnose | .2847 | 150 | 120 | 250 | 66.6 | 38.7 |
| Ketoxylose polymer[b] | .1149 | 75 | 30[a] | 61 | 7.2 | 4.99 |

[a] In a second 30-min. distillation period, 50 cc. was collected which contained no furfural. [b] Gross and Lewis, THIS JOURNAL, **53**, 2777 (1931).

**Tetramethylene Glycol and Tetrahydrofuran.**—This glycol was prepared from diethyl succinate by reduction with sodium and alcohol. The method was essentially that described by Müller.[20]

A solution of 2.79 g. of tetramethylene glycol in 150 cc. of 7.5 *N* sulfuric acid was refluxed during two hours. The reflux condenser was heated with water at 65–70°. The vapors passing over were condensed in a U-tube which was immersed in a freezing mixture. Two cc. of a liquid was collected which, after fractionation, yielded 1.7 g. of tetrahydrofuran. Due to its volatility, some was probably lost in manipulation, but even so the yield was 76%. Its boiling point was 64–65°, and its index of refraction, $n_D^{21}$ was 1.4043.

[20] Müller, *Monatsh.*, **49**, 27 (1928).

**Glycerol and Hydrochloric Acid.**—Ten grams of glycerol was refluxed for two hours with 100 cc. of 3.9 *N* hydrochloric acid. On cooling, the solution was neutralized. It gave no test for unsaturation with potassium permanganate solution, and it was without effect on hot Fehling's solution.

**Erythritol and Sulfuric Acid.**—Five grams of meso erythritol was refluxed with 100 cc. of 7.5 *N* sulfuric acid during six and one-half hours. The temperature of the reflux condenser was 35–50°. It was connected to a cold condenser and then to a U-tube which was immersed in a freezing mixture. No distillate of furan was collected.

Using a more concentrated sulfuric acid solution (50%, rather than 32%), Henninger[21] obtained a substance which he named erythran. Nothing of this type was found in the present study. After neutralizing the acid solution with barium carbonate and filtering off the barium sulfate, only unused erythritol was found. Three grams was recovered, and it is reasonable to assume that the remainder was lost in manipulation.

No furan was formed when erythritol and hydrochloric acid of varying concentrations to concentrated acid were refluxed together for several hours.

## Xylose, Sulfuric Acid and Salts

**Sodium Sulfate.**—A 7.7 *N* sulfuric acid solution was made by dissolving 45 cc. of 92% sulfuric acid in water which contained 75 g. of sodium sulfate. This solution, made up to 200 cc., boiled at 112°. One-tenth gram of xylose was added to it and three 250-cc. portions of distillate were collected in fifteen, fifteen and sixty minute periods. The furfural yields in these were 16.6, 15.6 and 33.1%, or a cumulative yield of 65.3%.

**Magnesium Sulfate.**—Seventeen cc. of 92% sulfuric acid was added to 135 cc. of a saturated aqueous solution of magnesium sulfate. It was, therefore, 3.9 *N* in acid. It boiled at 109.8–110°. Distillation of 0.1 g. of xylose from it in four periods of fifteen, fifteen, thirty and sixty minutes (distillation volumes of 150, 75, 200 and 200 cc.) yielded furfural, respectively, 5.3, 6.4, 13.8 and 20.7%; total yield, 46.2%.

When the effect of this 3.9 *N* acid solution (with magnesium sulfate) is compared with that of the 4.5 *N* acid (without magnesium sulfate, and therefore 7° lower boiling), it is seen that the furfural yield with the former is about double that with the latter. However, with 7.5 *N* acid (containing no magnesium sulfate), which boiled at 108.7°, the yield of furfural was considerably greater than with the aforesaid 3.9 *N* acid of b. p. 110°. These results illustrate the effect of temperature and of acid concentration.

**Xylose and a Butyric Acid Solution of Sulfuric Acid.**—Three cc. of concd. sulfuric acid was added to 150 cc. of butyric acid, thereby making a 0.67 *N* sulfuric acid solution with a boiling point of 162°. To it, 0.2836 g. of xylose was added and the mixture distilled from a 250-cc. flask. Butyric acid was added from a dropping funnel at about the same rate as it distilled away. The distillate was neutralized as it came over. In two and one-half hours, 205 cc. of distillate was collected. Only 3% of furfural was formed.

**Acetic Acid Solution of Benzenesulfonic Acid.**—Twenty grams of benzenesulfonic acid, 170 g. of glacial acetic acid and 0.1 g. of xylose in 5 cc. of water were distilled (118.5–121°) for half an hour. Acetic acid was constantly supplied as it distilled away. Only 1.1% yield of furfural resulted.

## Summary

A study has been made of the change of xylose into furfural. Dehydrating agents such as phosphorus pentoxide or anhydrous zinc chloride failed to promote this change. Solutions of phosphoric, trichloroacetic or nitric acid gave either no furfural or else gave very small yields of it. Both

[21] Henninger, *Ann. chim. phys.*, [6] **7**, 211 (1886).

hydrochloric and sulfuric acid solutions promoted furfural formation at distillation temperatures, the yield being dependent on the acid concentration, the temperature and on the duration of the distillation. This is a first order reaction.

The behavior of mineral acids at distillation temperatures on furfural, arabinose, rhamnose, tetramethylene glycol, ketoxylose, xylonic acid, glycerol and erythritol was investigated. In the last four cases there was little or no reaction. The significance of these results on the mechanism of the pentose-to-furfural reaction has been discussed.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

## SOME OBSERVATIONS ON THE FRIES REACTION[1]

BY F. F. BLICKE AND O. J. WEINKAUFF

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We became interested in the Fries reaction[2] because it seemed possible that this reaction might play a role in the formation of hydroxydiarylphthalides such as phenolphthalein. Furthermore, we wished to determine whether or not diphenyl phthalate, as well as phenyl 2-(*p*-hydroxybenzoyl)-benzoate, under the influence of aluminum chloride, would yield 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone.[3]

It has been stated by Rosenmund and Schnurr[4] that phenyl benzoate, when heated with aluminum chloride, is converted quantitatively into 4-hydroxybenzophenone. Similar results were obtained by us. We found that the benzoate of 4-hydroxydiphenyl behaves in an analogous manner to yield a compound which was, undoubtedly, 4-(*p*-hydroxyphenyl)-benzophenone since the material obtained by the action of aluminum chloride on the ester, after methylation, was identical with the substance prepared by condensation of benzoyl chloride with the methyl ether of 4-hydroxydiphenyl.

Csanyi[5] reported that diphenyl phthalate and aluminum chloride yield phenolphthalein but the amount of the latter which is produced and the experimental conditions which govern its formation were not recorded.

[1] This investigation was made possible by the establishment of the Michigan State Pharmaceutical Association Research Fund. We wish to express our appreciation for the aid which has been given us.

[2] A recent study of this reaction has been reported by Cox, THIS JOURNAL, **52**, 352 (1930).

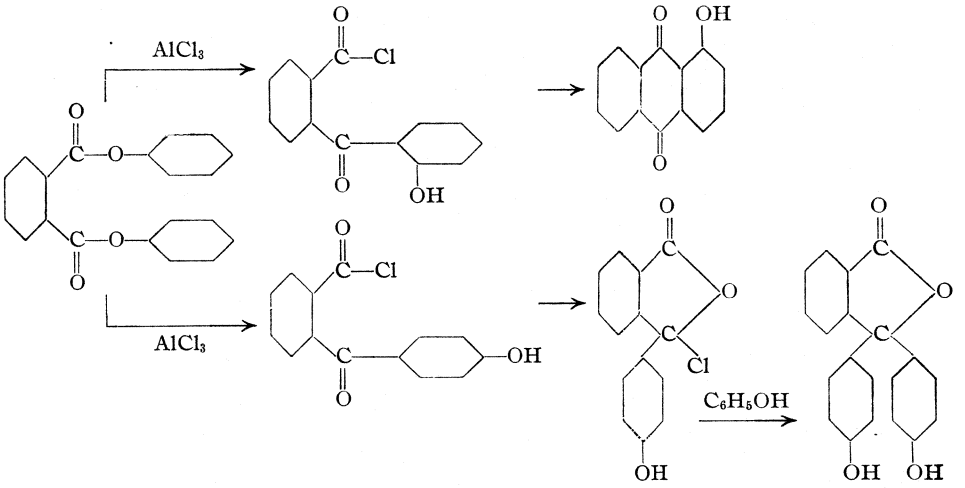
[3] This substance is isomeric with phenolphthalein and is easily obtained from it. The preparation of this compound is described by the authors in an article which will be published in an early issue of THIS JOURNAL.

[4] Rosenmund and Schnurr, *Ann.*, **460**, 89 (1928).

[5] Csanyi, *Ber.*, **52**, 1792 (1919).

We carried out a series of experiments with diphenyl phthalate and aluminum chloride and obtained mixtures of phenolphthalein and 1-hydroxyanthraquinone but were unable to isolate any of the substituted benzophenone. Csanyi makes no mention of an anthraquinone as a reaction product. Although the formation of an anthraquinone in this reaction is not surprising it would seem that a 2-hydroxy instead of a 1-hydroxy compound should be produced. The only explanation which we can offer to account for the formation of the latter substance is that some 2-(2′-hydroxybenzoyl)-benzoyl chloride may have been produced as an intermediate reaction product.

Phenyl 2-(methoxybenzoyl)-benzoate was changed, practically quantitatively, into phenolphthalein.




## Experimental Part

**Preparation of Esters.**—Phenyl benzoate was obtained in practically quantitative yield when benzoyl chloride and phenol, mixed in equivalent amounts, were allowed to remain at ordinary temperature for several hours. The ester was washed with alcohol and then recrystallized from the same solvent; m. p. 69–70°.

Diphenyl phthalate was prepared from phthalyl chloride and phenol in the manner described above. After recrystallization from alcohol it melted at 74–76°.

In order to obtain the benzoate of 4-hydroxydiphenyl, benzoyl chloride and 4-hydroxydiphenyl were mixed and kept in a molten state until no more hydrogen chloride was evolved. The ester melted at 150–151° after recrystallization from alcohol.

Phenyl 2-(*p*-methoxybenzoyl)-benzoate was prepared in the following manner. Forty-eight grams of 2-(*p*-hydroxybenzoyl)-benzoic acid was methylated with 160 cc. of 10% sodium hydroxide solution and 40 cc. of dimethyl sulfate. A portion of the methyl ester of 2-(*p*-methoxybenzoyl)-benzoic acid, which separated as a crystalline solid, was removed from the methylation mixture and recrystallized from methyl alcohol; m. p. 82–83°.[6] Sixteen grams of sodium hydroxide was added to the reaction

[6] Egerer and H. Meyer [*Monatsh.*, **34**, 80 (1913)] recorded the melting point as 83°.

mixture and the latter heated for three hours on a steam-bath in order to hydrolyze the methyl ester. When the mixture was cooled a crystalline precipitate formed, presumably the sodium salt of the substituted benzoic acid. The latter was removed by filtration and the precipitate and filtrate acidified separately. The 2-(*p*-methoxybenzoyl)-benzoic acid was recrystallized from dilute alcohol; m. p. 146–147°.[7]

In order to prepare the acid chloride, 31 g. of the acid and 29 g. of thionyl chloride were mixed and allowed to remain at ordinary temperature for twelve hours. The excess thionyl chloride was removed under diminished pressure at ordinary temperature, the residue dissolved in absolute ether and the ether distilled under reduced pressure. The treatment with ether was continued until practically all of the thionyl chloride had been removed. The acid chloride was obtained in the form of a viscous oil.

Twenty-five grams of the crude chloride and potassium phenolate, prepared from 10.3 g. of phenol, 4.1 g. of potassium and 300 cc. of absolute ether, were heated for one hour on a steam-bath. After recrystallization from alcohol the phenyl 2-(*p*-methoxybenzoyl)-benzoate melted at 144–145°. The same ester was obtained from the acid chloride prepared with the aid of phosphorus pentachloride.

*Anal.* Calcd. for $C_{21}H_{16}O_4$: C, 75.88; H, 4.86. Found: C, 75.65; H, 4.86.

One and sixty-six hundredths grams of the ester was hydrolyzed and the phenol formed converted into tribromophenol. There was obtained 1.25 g. of 2-(*p*-methoxybenzoyl)-benzoic acid and 1.57 g. of tribromophenol; the calculated amounts of acid and tribromophenol are 1.28 g. and 1.65 g., respectively.

**Reaction of Esters with Aluminum Chloride. Phenyl Benzoate.**—Five grams of phenyl benzoate was heated with aluminum chloride according to the directions of Rosenmund and Schnurr.[4] 4-Hydroxybenzophenone was obtained in quantitative yield; m. p. 135–136°.

**Benzoate of 4-Hydroxydiphenyl.**—Five grams of the ester, 3 g. of aluminum chloride and 25 cc. of tetrachloroethane were heated for one hour in a bath at 140°. The mixture was decomposed with ice and hydrochloric acid and then steam distilled to remove the solvent. The residue was boiled with sodium hydroxide solution, filtered and the filtrate acidified. The gummy precipitate was dried and dissolved in hot benzene. The crystals which were obtained from the solution were recrystallized from alcohol; m. p. 193–195°. This material, 4-(*p*-hydroxyphenyl)-benzophenone, was methylated with dimethyl sulfate. The methyl ether melted at 168–169° after recrystallization from alcohol.

4-(*p*-Methoxyphenyl)-benzophenone was synthesized in the following manner. Nine grams of 4-methoxydiphenyl,[8] 7 g. of benzoyl chloride, 8 g. of aluminum chloride and 40 cc. of carbon disulfide were allowed to remain at ordinary temperature for twenty-four hours. The carbon disulfide was decanted, the mixture treated with ice and hydrochloric acid and then subjected to steam distillation. The residue was dissolved in benzene and shaken with sodium hydroxide solution a number of times. Upon evaporation of the benzene a yellow, crystalline product was obtained. After several recrystallizations from alcohol the compound was obtained in a colorless state; m. p. 168–169°. Mixed with the methylated product obtained from the Fries reaction the melting point was found to be that given above.

**Diphenyl Phthalate.**—Ten grams of diphenyl phthalate, 10 g. of aluminum chloride and 25 cc. of tetrachloroethane were heated at 100° for six hours. After the addition of hydrochloric acid the mixture was subjected to steam distillation. After all of the tetrachloroethane had been removed a small amount of yellow, crystalline material separated in the condenser. This substance was, undoubtedly, impure 1-hydroxy-

[7] Meyer and Turnau [*Monatash.*, **30**, 487 (1909)] recorded the melting point as 148°.

[8] Werner, *Ann.*, **322**, 167 (1902).

anthraquinone; m. p. 180–200°. The residue in the steam distillation flask was treated with 120 cc. of 10% sodium hydroxide solution, the alkali-insoluble material, which weighed 3 g., removed by filtration and the filtrate acidified. The precipitated material was recrystallized from acetic acid. This proved to be phenolphthalein. The yield was 3 g., m. p. 253–255°. The alkali-insoluble product, after recrystallization from alcohol, was obtained in the form of yellow needles; m. p. 194–195°. This material was 1-hydroxyanthraquinone; mixed m. p. 196–198°.[9] The hydroxyanthraquinone obtained as a reaction product was acetylated[10] and mixed with pure acetylated 1-hydroxyanthraquinone. The mixed melting point, 185–187°, was that of pure acetyl-1-hydroxyanthraquinone.

In another experiment 10 g. of diphenyl phthalate, 10 g. of aluminum chloride and 25 cc. of tetrachloroethane were heated at 150° for thirty minutes. There were obtained 2.3 g. of 1-hydroxyanthraquinone and 6.3 g. of phenolphthalein.

**Phenyl 2-(*p*-Methoxybenzoyl)-benzoate.**—Two grams of the ester, 2 g. of aluminum chloride and 10 cc. of tetrachloroethane were heated for two hours at 90°. After decomposition and steam distillation of the reaction mixture the residue was dissolved in alkali and the solution acidified. After recrystallization from acetic acid the phenolphthalein obtained melted at 256–257°. The yield of pure material was 1.7 g.; the calculated amount is 1.9 g. The phenolphthalein is probably formed as a result of the formation of the following intermediate products: (a) 2-(*p*-methoxybenzoyl)-benzoyl chloride, *p*-methoxyphenylchlorophthalide or (b) *p*-methoxyphenylphenoxyphthalide. It is impossible to state at which stage during the process demethylation takes place.

**Separation of Phenolphthalein from 2-Hydroxyanthraquinone.**—Since it was considered possible that some 2-hydroxyanthraquinone might be formed from the action of aluminum chloride on diphenyl phthalate, the reaction products were carefully examined for this anthraquinone. However, we were unable to obtain any of the 2-hydroxy compound.

The separation of 1-hydroxyanthraquinone from phenolphthalein is not a difficult matter since the former substance does not dissolve readily in 10% sodium hydroxide solution. However, 2-hydroxyanthraquinone is readily soluble in aqueous sodium hydroxide, hence the following procedure was used in the case of reaction mixtures which we thought might consist of phenolphthalein and 2-hydroxyanthraquinone. The process is illustrated by the separation of a mixture prepared from 2.5 g. of phenolphthalein and an equal amount of 2-hydroxyanthraquinone. After the material had been dissolved in 60 cc. of 10% sodium hydroxide solution, 3 g. of zinc dust was added and the mixture heated for one hour on a steam-bath. The excess zinc was removed by filtration and the filtrate acidified with hydrochloric acid. The precipitated material was washed with water and then digested with 150 cc. of 5% sodium bicarbonate solution. The insoluble material, reduced hydroxyanthraquinone, was removed by filtration and the filtrate acidified. The precipitated material was dissolved in 25 cc. of hot alcohol and the solution mixed with 150 cc. of hot water. After some time phenolphthalein (4',4''-dihydroxytriphenylmethane-2-carboxylic acid) separated in the form of needles, m. p. 233–234°, yield 2.4 g. or 96% of the calculated amount. Phenolphthalin can be converted readily into phenolphthalein by oxidation.[11] The crude, re-

[9] An unusually pure sample of 1-hydroxyanthraquinone which we prepared from 1-aminoanthraquinone melted at 200–201°. The highest melting point recorded for this compound in the literature is 193° [Ullmann, *Ber.*, **53**, 829 (1920)]. It was found that 2-hydroxyanthraquinone, prepared from 2-hydroxyanthrone-9, melts at 303–304°. Decker and Laube [*ibid.*, **39**, 113 (1906)] recorded the melting point as 306° (corr.).

[10] Dimroth, Friedmann and Kämmerer, *ibid.*, **53**, 482 (1920).

[11] Baeyer, *Ann.*, **202**, 82 (1880).

duced hydroxyanthraquinone weighed 1.7 g. Oxidation of this material with sodium dichromate in acetic acid solution yielded an impure hydroxyanthraquinone. It seems probable, however, that a suitable oxidation process might be found whereby pure 2-hydroxyanthraquinone could be obtained from the reduction product.

## Summary

The benzoate of 4-hydroxydiphenyl, when heated with aluminum chloride, yields 4-(*p*-hydroxy-phenyl)-benzophenone. Diphenyl phthalate, treated in a similar manner, is converted into phenolphthalein and 1-hydroxyanthraquinone. Phenyl 2-(methoxybenzoyl)-benzoate is changed quantitatively by aluminum chloride into phenolphthalein.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 678]

# SOME ALPHA-ALKYLCINNAMIC ACIDS AND THEIR DERIVATIVES

BY MARSTON TAYLOR BOGERT AND DAVID DAVIDSON[1]

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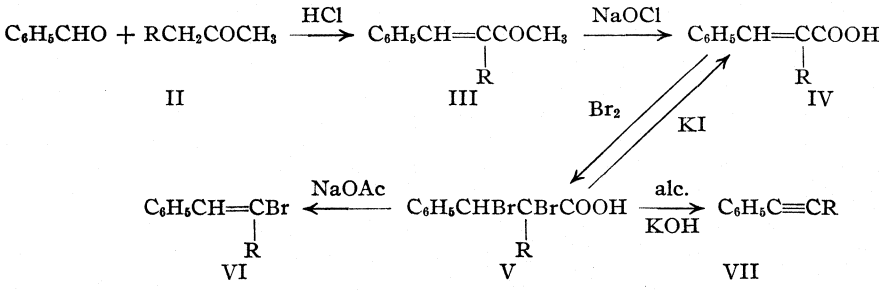
## Introduction

The phenomenal success of α-amylcinnamic aldehyde and other α-alkylcinnamic aldehydes as perfume bases, led us to prepare several of the corresponding methyl ketones (methyl-(α-alkyl-)-styryl ketones) (III). These were synthesized by condensing benzaldehyde with alkyl acetones (II) by means of hydrogen chloride. The methyl (α-alkyl-)-styryl ketones are readily converted to the α-alkylcinnamic acids (IV) by means of sodium hypochlorite. The acids, in turn, are of interest, since, through their dibromides (V), they may be transformed into the β-alkyl-β-bromostyrenes (VI), or into the alkylphenylacetylenes (VII).




The dibromides are also readily reconverted to the α-alkylcinnamic acids by means of potassium iodide.

Since the α-alkyl cinnamic acids obtained were of the *trans* configuration

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(absence of indone formation with sulfuric acid),[2] we may assign the *trans* configuration (VIII) to the corresponding ketones[3] $\begin{matrix} C_6H_5—CH \\ \| \\ RCCOCH_3 \end{matrix}$.

Ethyl, *n*-propyl, *n*-butyl and *n*-amyl derivatives are reported in this paper. The attempt to prepare the isopropyl derivatives by starting with isopropyl acetone, $(CH_3)_2CHCH_2COCH_3$, gave an anomalous result, since it was not found possible to prepare a solid oxime from the supposed methyl (α-isopropyl-)-styryl ketone, nor to oxidize it to α-isopropylcinnamic acid.[4] In this connection it is interesting to note that the application of the Perkin synthesis to the preparation of α-isopropylcinnamic acid gives only a very small yield of that acid besides considerable β-isopropylstyrene.[5]

## Experimental

TABLE I

METHYL (α-ALKYL-)-STYRYL KETONES

| R | Reference | B. p., °C. (Mm.) | Analysis Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found | M. p. of oxime,[a] °C. | Nitrogen in oxime Calcd. | Nitrogen in oxime Found |
|---|---|---|---|---|---|---|---|---|---|
| H | *Ann.*, **294**, 275 (1897) | 151–153 (25) | | | | | 115–116 | | |
| $CH_3$ | *Ber.*, **35**, 970 (1902) | 127–130 (12) | | | | | 103–104 | | |
| $C_2H_5$ | *Ber.*, **35**, 3090 (1902) | 120–130[b] (18) | | | | | 85 | | |
| *n*-$C_3H_7$ | This paper | 142–143 (14) | 83.0 | 82.3 | 8.5 | 8.7 | 70 | 6.9 | 6.3 |
| *n*-$C_4H_9$ | This paper | 155–156 (15) | 83.2 | 82.7 | 8.9 | 9.1 | 61 | 6.5 | 6.2 |
| *n*-$C_5H_{11}$ | This paper | 161–162 (14) | 83.3 | 82.7 | 9.3 | 9.3 | 71 | 6.1 | 5.8 |

[a] Prepared by the method of Harries and deOsa, *Ber.*, **36**, 2998 (1903). [b] This paper, 144–145° (22 mm.).

One-half mole of benzaldehyde was mixed with one mole of the alkyl acetone[6] and one-fourth mole of hydrogen chloride gas passed into the cooled mixture. The mixture, which soon became red, was then shaken for sixteen to twenty hours. At the end of this time the water formed in the reaction had separated as aqueous hydrochloric acid and was removed. Without further treatment, the oil was distilled under diminished pressure (about 20 mm.). Somewhat more than half of the alkyl acetone was recovered and a small residue, probably consisting of dibenzal-alkyl acetone (styryl-(α-alkyl-)-styryl ketone), remained in the flask. The principal fraction, consisting of crude methyl (α-alkyl-)-styryl ketone, was obtained in a yield of about 90% based on the alkyl acetone consumed, or about 75% based on the benzaldehyde employed. The crude

[2] Stoermer and Voht, *Ann.*, **409**, 55 (1915).

[3] See Bogert and Davidson, THIS JOURNAL, **53**, 3122 (1931), for a discussion of the configuration of α-amylcinnamic aldehyde.

[4] According to Gheorghiu and Arwentiew, *J. prakt. Chem.*, [2] **118**, 295 (1928), the condensation product obtained by the action of hydrogen chloride on a mixture of benzaldehyde and isopropyl acetone has the constitution $C_6H_5CH=CHCOCH_2CH(CH_3)_2$ rather than $C_6H_5CH=\underset{\displaystyle CH(CH_3)_2}{\overset{\displaystyle |}{C}}COCH_3$.

[5] Schaarschmidt, Georgeacopol and Herzenberg, *Ber.*, **51**, 1059 (1918).

[6] Ethyl acetone was prepared by the oxidation of methyl propyl carbinol. Propyl and amyl acetones were purchased from Akatos, Inc. Butyl acetone was synthesized according to "Organic Syntheses," **7**, 60 (1927).

alkyl acetone fraction was treated with one-half mole of benzaldehyde and sufficient alkyl acetone to replace that consumed in the first reaction. Hydrogen chloride was then added and the reaction carried out as before. The process was repeated three times but could probably be carried on indefinitely. By using two moles of alkyl acetone to one of benzaldehyde and reworking the recovered alkyl acetone in this way, the amount of dibenzal derivative formed was greatly reduced, with consequent improvement in the yield of the desired product. The crude methyl ($\alpha$-alkyl-)-styryl ketone may be used directly for the preparation of the $\alpha$-alkylcinnamic acids. To purify it, the crude product was washed with saturated sodium bisulfite, followed by water and then treated with alcoholic potassium hydroxide, thrown into water, acidified with acetic acid, extracted with benzene, dried over sodium sulfate and distilled. A middle fraction was taken for analysis. The methyl ($\alpha$-alkyl-)-styryl ketones are liquids having a greenish-yellow tinge, with a floral odor which resembles, but is much weaker than, that of the $\alpha$-alkylcinnamic aldehydes.

TABLE II

*Trans*-$\alpha$-ALKYLCINNAMIC ACIDS

| R | Reference | M. p., °C. | Equivalent Weight Calcd. | Equivalent Weight Found | Analysis Carbon Calcd. | Analysis Carbon Found | Analysis Hydrogen Calcd. | Analysis Hydrogen Found |
|---|---|---|---|---|---|---|---|---|
| H | Ger. Pat. 21,162 (1882) | 133 | | | | | | |
| $CH_3$ | *Ber.*, **35**, 3552 (1902) | 81–2 (74 mm.) | | | | | | |
| $C_2H_5$ | *Ann.*, **409**, 57 (1915) | 104–105 (this paper, 107°) | | | | | | |
| *n*-$C_3H_7$ | This paper | 93 | 190 | 190 | 75.8 | 75.8 | 7.4 | 7.3 |
| *n*-$C_4H_9$ | *Ber.*, **34**, 929 (1901) | 83–84 | | | | | | |
| *n*-$C_5H_{11}$ | This paper | 80 | 218 | 218 | 77.0 | 77.0 | 8.3 | 8.2 |

To one-tenth mole of crude methyl ($\alpha$-alkyl-)-styryl ketone dissolved in 200 cc. of alcohol and chilled in a freezing mixture was added with stirring a solution of one mole of sodium hydroxide in 100 cc. of water into which three-tenths mole of chlorine had been passed in the cold. The temperature was kept below 20°, the addition requiring about fifteen minutes. The mixture was then stirred for an hour at room temperature. At this stage two layers were present as well as some solid salt. The mixture was distilled, chloroform coming over first, then alcohol and water and finally some oily material. About 250 cc. of distillate was collected. The residue separated into two layers, an aqueous layer and one consisting of the molten sodium $\alpha$-alkylcinnamate. On cooling, the latter solidified and was removed. This was dissolved in several hundred cc. of boiling water, the solution clarified with Norite and finally acidified with hydrochloric acid. Fine white needles of the $\alpha$-alkylcinnamic acid separated. Recrystallization from 75% acetic acid gave an odorless, colorless product; yield, about 80%. For analysis, the acids were recrystallized several times from 75% acetic acid and then several times from dilute alcohol.

TABLE III

$\alpha$-ALKYLCINNAMIC ACID DIBROMIDES (HIGHER MELTING FORMS)

| R | Reference | M. p., °C. | Analysis Carbon Calcd. | Analysis Carbon Found | Analysis Hydrogen Calcd. | Analysis Hydrogen Found |
|---|---|---|---|---|---|---|
| H | *J. Chem. Soc.*, **83**, 669 (1903) | 203–204 | | | | |
| $CH_3$ | *Ber.*, **21**, 276 (1889) | 137 | | | | |
| $C_2H_5$ | This paper | 99–100 | 39.3 | 39.4 | 3.6 | 3.6 |
| *n*-$C_3H_7$ | This paper | 149–150 | 41.3 | 40.7 | 4.0 | 4.0 |
| *n*-$C_4H_9$ | This paper | 109–110 | 42.9 | 43.1 | 4.4 | 4.3 |
| *n*-$C_5H_{11}$ | This paper | 143–144 | 44.5 | 43.7 | 4.8 | 4.6 |

According to the method of Sudborough and Thompson[7] one-tenth mole of finely pulverized α-alkylcinnamic acid was placed in a wide-mouthed glass-stoppered bottle, into which was lowered a test-tube containing 0.11 mole of bromine. The bottle was sealed and allowed to stand for one to two weeks. During this time the solid was occasionally turned over to expose it more thoroughly to the action of the bromine vapor. The gain in weight of the acid was almost theoretical. The slightly sticky solid was triturated with petroleum ether, filtered and washed with petroleum ether. A pulverulent solid, melting about ten degrees below the pure dibromide was obtained in yields of from 75 to 90%. After several crystallizations from carbon tetrachloride + petroleum ether, it was obtained in dense sugar-like crystals of constant melting point.

**Reduction of the α-Alkylcinnamic Acid Dibromides.**—0.01 Mole of the dibromide was refluxed for twenty minutes with 0.04 mole of potassium iodide in 25 cc. of alcohol. The mixture was thrown into dilute sodium bisulfite. The theoretical quantity of crude acid was obtained, which when recrystallized from 75% acetic acid gave the pure α-alkylcinnamic acid; yield, 75%.

TABLE IV

β-ALKYL β-BROMOSTYRENES

| R | Reference | B. p., °C. (Mm.) | Analysis Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|
| H | *Ber.*, **42**, 2878 (1909) | 218–220 | | | | |
| $CH_3$ | *Ber.*, **21**, 276 (1889) | 226 | | | | |
| $C_2H_5$ | This paper | 126–128 (23) | 56.8 | 57.2 | 5.2 | 5.5 |
| $n$-$C_3H_7$ | This paper | 138–140 (22) | 58.7 | 59.3 | 5.8 | 5.9 |
| $n$-$C_4H_9$ | This paper | 148–150 (20) | 60.2 | 60.7 | 6.3 | 6.6 |
| $n$-$C_5H_{11}$ | This paper | 161–162 (18) | 61.6 | 61.9 | 6.7 | 6.8 |

One-tenth mole of α-alkylcinnamic acid dibromide, 100 cc. of alcohol and 0.11 mole of sodium acetate trihydrate were heated by means of an air-bath in a bulb attached to an empty upright bulb condenser, which, in turn, was connected to a downward condenser. The reaction took place immediately with the evolution of carbon dioxide and the separation of sodium bromide. The heating was continued until 90 cc. of alcohol had been recovered. Brine was then added to the residue and the product steam distilled, the water in the condensate being returned to the boiler. The oil was separated and dried; yield of crude, about 85%. The bromostyrenes are greenish-tinged oils which are heavier than water, and possess a harsh floral odor.

TABLE V

ALKYLPHENYLACETYLENES

| R | Reference | B. p., °C. (Mm.) | Analysis Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|
| H | THIS JOURNAL, **44**, 425 (1922) | 142–143 | | | | |
| $CH_3$ | *Ber.*, **21**, 276 (1889) | 185 | | | | |
| $C_2H_5$ | *J. Chem. Soc.*, **29**, 162 (1876) | 201–203 | | | | |
| $n$-$C_3H_7$ | This paper | 102–103 (18.5) | 91.7 | 90.9 | 8.3 | 8.5 |
| $n$-$C_4H_9$ | This paper | 119–121 (18) | 91.1 | 91.1 | 8.9 | 8.8 |
| $n$-$C_5H_{11}$ | This paper | 126–127 (15) | 90.7 | 89.9 | 9.3 | 9.0 |

Earlier methods of preparation for this group involved the alkylation of phenylacetylene or the dehalogenation of a halostyrene. The following procedure yielded the alkylphenylacetylene directly from the cinnamic acid dibromide.

[7] Sudborough and Thompson, *J. Chem. Soc.*, **83**, 669 (1903).

One-tenth mole of α-alkylcinnamic acid dibromide (or the crude product obtained by adding one-tenth mole of bromine to one-tenth mole of α-alkylcinnamic acid in carbon tetrachloride and then evaporating the carbon tetrachloride with a current of air) was gradually added to a solution of 0.7 mole of potassium hydroxide in 100 cc. of alcohol. Sufficient heat was evolved to cause the mixture to boil. Most of the alcohol was then removed with the aid of a column. Water was added to the residue and the product steam distilled, the water in the distillate being returned to the boiler. The oil was separated and dried; yield of crude, about 70%. These acetylenes are colorless oils, lighter than water, with a "green-leaf" odor resembling methyl heptine carbonate.

**Acknowledgments.**—The authors are indebted to Mr. Richard O. Roblin, Jr., for the synthesis of butyl acetone, to the Florasynth Laboratories for a gift of benzaldehyde, to the Sharples Solvents Corp. for a gift of methyl propyl carbinol and especially to the American Manufacturers of Toilet Articles and the National Academy of Sciences for financial aid.

## Summary

Condensation of benzaldehyde with ethyl, *n*-propyl, *n*-butyl and *n*-amyl acetone yielded the corresponding methyl (α-alkyl-)-styryl ketones, which were converted into the α-alkylcinnamic acids by means of sodium hypochlorite. These acids, through their dibromides, were converted into the β-alkyl-β-bromostyrenes and the alkylphenylacetylenes.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON]

# THE OZONIDES OF ORTHO-XYLENE AND THE STRUCTURE OF THE BENZENE RING[1]

BY A. A. LEVINE AND A. G. COLE[2]

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## Introduction

The problem of the existence and the position of ethylenic linkages in benzene with the possibility of the existence of isomeric ortho-disubstitution products has been the subject of many interesting speculations ever since Kekulé[3] advanced his theory of the structure of the benzene nucleus. Some results have been published[4] which indicate the occurrence of such isomers.

Harries and his co-workers[5] have described osazone derivatives of the decomposition products of ozonides of benzene and mesitylene. It seemed

[1] Presented before the Organic Division of the American Chemical Society at its 80th meeting in Cincinnati, 1930.

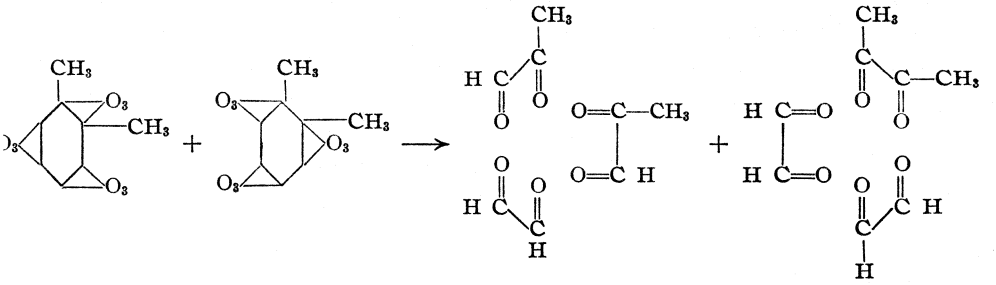
[2] Abstract of a thesis presented to the Graduate Faculty by A. G. Cole in partial fulfilment of the requirements for the degree of Master of Science.

[3] Kekulé, *Ann.*, **137**, 158 (1866).

[4] Borsche and Bahr, *ibid.*, **402**, 81 (1913); Hodgson, *Chem. Abstracts*, **21**, 572 (1927).

[5] Harries, "Ozone and seine Einwirkung," Julius Springer, Berlin, **1916**.

evident that similar results could be obtained by ozonizing *o*-xylene and obtaining derivatives of the decomposition products. Assuming that a conjugated arrangement of the double bonds in its nucleus does occur, *o*-xylene should, theoretically, be convertible into two ozonides because of the position of its two methyl groups. These two ozonides should produce three products upon decomposition with water, whereas, in the cases of benzene and mesitylene, only one decomposition product is possible in each case. The following scheme shows the two possible ozonides and their three decomposition products.



A B A′ B′

The same decomposition products would be possible if the two structures of *o*-xylene pictured above merely represented phases of some complex dynamic structure which may actually exist, since the process of ozonization would tend to stabilize these two phases. Accordingly *o*-xylene was subjected to the action of 15% ozone and a product obtained which when decomposed with water yielded derivatives of the above three decomposition products: glyoxal, methylglyoxal and dimethylglyoxal or diacetyl. Since these decomposition products are possible only in the event that two ozonides were previously formed, it follows that there were present in *o*-xylene, the above two structures or their equivalents.

The osazones and *p*-nitrophenylosazone derivatives of the above three decomposition products were all isolated, with the exception of methylglyoxal osazone, and identified by their melting points and mixed melting point determinations with authentic specimens. A small quantity of material which was apparently diacetyl was also isolated.

Various solvents for *o*-xylene were tried during ozonization. With petroleum ether, an insoluble product in the form of small transparent crystals was obtained. These were very explosive when removed from the ether. With acetic acid and acetic anhydride, a clear yellow solution was obtained which was decomposed by pouring onto cracked ice. Acetic anhydride was found to be the best solvent since it ensures an anhydrous medium and both itself and its hydrolysis product, acetic acid, are not acted upon by ozone.

Two methods for isolating the osazone derivatives of the decomposition products were employed. The first method was to treat the decomposition mixture with a solution of phenylhydrazine acetate or *p*-nitrophenylhydrazine hydrochloride and isolate the individual derivatives by a process of fractional crystallization. The second and most satisfactory method was roughly to separate the three decomposition products by steam distillation before the conversion into the above derivatives.

When the decomposition mixture of the ozonides was distilled and the first fourth of the distillate repeatedly distilled in the presence of 15% sulfuric acid, a small amount of a liquid was finally obtained which was apparently diacetyl.

## Experimental

All melting points given herein are uncorrected.

The ozonizing apparatus used for all experiments was essentially that described by Levine.[6] This apparatus gave a 15% concentration of ozone when oxygen was used.

The *o*-xylene used in the experiments was obtained from the Eastman Kodak Company. Its melting point was −28° and its boiling point 142 ± 0.1°.

**Ozonization of *o*-Xylene in Various Solvents.**—A solution of 3 g. of *o*-xylene in 15 g. of petroleum ether was cooled to −25 to −30° and ozone passed through for twenty-four hours. A transparent precipitate of fine crystals separated from the solution. It was explosive when removed from the solvent.

When acetic anhydride was used in place of petroleum ether, 3 g. of *o*-xylene was dissolved in 15 cc. of acetic anhydride, cooled to −30° and ozonized with 15% ozone for three to four hours. The acetic anhydride dissolves the ozonides of *o*-xylene and hence no precipitate was formed.

**Isolation of Glyoxal and Diacetyl Osazones.**—An acetic anhydride solution of *o*-xylene was ozonized as described above and the resulting product was decomposed by stirring it with crushed ice. The three decomposition products were roughly separated from each other by a process of fractional steam distillation. Upon distilling the water solution of these products, the first fraction, about one-fourth of the original volume, contained most of the diacetyl since this substance is very volatile with steam. Methylglyoxal, which is considerably less volatile with steam, was obtained in the second fraction, one-half the original volume. The non-volatile glyoxal remained in the residue.

When the first fraction was treated with phenylhydrazine acetate, a flocculent precipitate formed. By recrystallizing this material several times from benzene (or alcohol), clear yellow flakes were obtained which melted at 238–239°. The substance was identified as diacetyl osazone by a mixed melting point determination.

By treating the second fraction with phenylhydrazine acetate, a dark oil was formed from which it was impossible to isolate a crystalline product.

The residue upon similar treatment, gave a precipitate which recrystallized from benzene or alcohol in the form of yellow flaky crystals; m. p. 167–168°. The substance was identified by a mixed melting point determination.

[6] Levine, *Northwest Science*, **3**, 19 (1929).

**Isolation of *p*-Nitrophenylosazones of Glyoxal, Methylglyoxal and Diacetyl.**—Two methods were employed in isolating these products. One method was to first roughly to separate the decomposition products of the ozonides by fractionally distilling the decomposition mixture as described above and then treating each of the three fractions obtained with *p*-nitrophenylhydrazine hydrochloride. The first portion of the distillate gave a substance which after recrystallization from nitrobenzene as fine red needle-shaped crystals, melted at 313°. Small dull red crystals purified by recrystallization from dimethylaniline and which melted at 284–285° were obtained from the second fraction. The residue which contained glyoxal in the polymerized form gave a precipitate with *p*-nitrophenylhydrazine hydrochloride which melted at 309–310° after the material was recrystallized from nitrobenzene as fine, red needle-shaped crystals. The first product was identified as diacetyl-*p*-nitrophenylosazone, the second as methylglyoxal-*p*-nitrophenylosazone and the last as glyoxal-*p*-nitrophenylosazone by mixed melting point determinations with authentic compounds.

A second method of isolation used was to treat the mixture of decomposition products with *p*-nitrophenylhydrazine hydrochloride directly and then to selectively dissolve from the dried precipitated material, one product at a time by the use of suitable solvents. By extracting the mixture of products with pyridine, diacetyl-*p*-nitrophenylosazone was roughly isolated since the other two products are comparatively insoluble in this solvent. It was purified by repeated crystallizations. The residue after this extraction was then extracted with dimethylaniline. From the dimethylaniline portion methylglyoxal-*p*-nitrophenylosazone was isolated. By recrystallizing the material remaining after these two extractions several times from benzene, the *p*-nitrophenylosazone of glyoxal was obtained. In each of these cases the substance was identified by the method used above.

**Isolation of Diacetyl as a Decomposition Product of the Ozonides.**—Distillation of the mixture obtained by decomposing the ozonized product with ice, then repeatedly distilling the first one-fourth of the distillate in the presence of 15% sulfuric acid, gave a small quantity of liquid which was apparently diacetyl. Although there was not sufficient material to permit of proper purification, its boiling point was within the range of that for diacetyl. Its color, odor, miscibility with water and behavior during distillation from a water solution checked well with the corresponding properties of diacetyl.

## Summary

1. *o*-Xylene was ozonized in various solvents, acetic anhydride being found the most suitable.

From the mixture obtained by decomposing the ozonization products with ice, phenylhydrazine derivatives of glyoxal and diacetyl and *p*-nitrophenylhydrazine derivatives of glyoxal, methylglyoxal and diacetyl were isolated. A small quantity of a substance which was apparently diacetyl was likewise isolated.

2. Since three decomposition products were obtained it appears as if *o*-xylene exists in two isomeric configurations.

NIAGARA FALLS, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO]

# STUDIES IN PROTEINS. III. THE UNIFORM SOLUBILITY OF THE PROTEIN FRACTION OF ORANGE SEED MEAL IN SOLUTIONS OF VARIOUS SODIUM SALTS[1]

BY LOUISE KNIGHT ROTHA AND FELIX SAUNDERS

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## Introduction

The solubility of certain proteins in neutral salt solutions was first observed by Denis[2] in 1859. The method received little attention until 1876 when Weyl[3] used it in extracting seeds from which he obtained a product which resembled the globulins found in animal tissues. Previously, Ritthausen[4] had obtained products similar to these plant globulins by extraction with dilute alkaline solutions, but it was maintained by Weyl that these products differed from globulins. Ritthausen, however, was able to show that the compounds which he obtained were similar whether extracted by weakly alkaline solutions or by neutral salt solutions. The value of his work was still questioned.

Because of the confusion that existed in reports on vegetable proteins, T. B. Osborne[2] undertook an extensive study of the subject and as a result has given us much information concerning the plant globulins. In practically all of the studies of Osborne and of the other workers in the field, sodium chloride was used in various concentrations as the extracting agent. In 1905 Osborne and Harris[5] determined the solubility of proteins in solutions of various salts. Edestin was used as a typical crystalline globulin. It was observed that the chlorides of univalent metals such as sodium and potassium had practically the same power to dissolve the edestin, while the chlorides of divalent metals extracted about twice as much as those of the univalent. A normal solution of sodium sulfate dissolved the globulin readily, while a molar solution dissolved very little. Sodium and potassium iodides were alike in having the greatest solvent effect on the protein. It was also observed that the basic salts in general had a greater solvent power than the acid salts.

Other workers than Osborne have investigated the solvent effect of various salts and have obtained varied results depending upon the salt

[1] From the thesis presented by Louise Knight Rotha in partial fulfilment of the requirements for the degree of Master of Science, 1931.

[2] P. S. Denis, *Mémoire sur le sang*, etc. (1858) as quoted in T. B. Osborne, "The Vegetable Proteins," Longmans, Green and Co., New York, **1919**, p. 21.

[3] T. Weyl, *Z. physiol. Chem.*, **1**, 72–100 (1877).

[4] H. Ritthausen, *Pfluger's Archiv.*, **15**, 269–288 (1877); **21**, 81–104 (1880).

[5] T. B. Osborne and I. F. Harris, *Am. J. Physiol.*, **14**, 151–171 (1905).

used, the concentration of the solution, the material being studied, and various other factors. Particularly outstanding in this connection are the studies of Gortner[6] and his co-workers. In an experiment on twelve kinds of wheat flour it was observed that the salt solutions of various concentrations showed a difference in their solvent or "peptizing" action toward the proteins. A definite lyotropic series was noted. From this they concluded that such effects were due to the properties of both of the cations and the anions of the salts, and that apparently none of the salts used was extracting a chemical entity that could be designated as a globulin.

In a more recent work, Gortner and Staker[7] have observed a lyotropic series in the case of many seeds. However, with sorghum, millet, corn and teosinte there was little evidence of a lyotropic series of anions, in fact sorghum showed none at all.

In 1929 Saunders[8] isolated from orange seed meal a crystalline globulin, pomelin. He obtained this globulin by extracting the meal with a warm solution of salt. Extractions of the meal were made with normal solutions of the chlorides, bromides and iodides of lithium, sodium and potassium with quite uniform results. The salt solutions were found to be extracting repeatedly an average of 73.4% of the total nitrogen of the meal. He concluded that there was no evidence for the existence of a lyotropic series in the extracting power of the different alkali halides on orange seed meal.

With such uniform results shown by the extraction of pomelin with normal solutions of alkali halides, a study of the extracting ability of other normal salt solutions was undertaken. The following pages give the results of these experiments.

**Material.**—Orange seed meal which contains the globulin, pomelin, was used. This material had been obtained by grinding the whole orange seeds[9] and removing the oil with benzene. The meal after being air-dried was sifted and the 20–40 mesh portion was used. Normal solutions of salts of high chemical purity were used for the extractions.

**Method.**—A 6-g. sample of the orange seed meal was mixed with 50 cc. of the salt solution being studied in a 250-cc. centrifuge bottle. This was shaken for twenty minutes in a mechanical shaker, centrifuged for twenty minutes until the material was well packed and then the supernatant liquid was filtered through cotton into a Kjeldahl flask. The solution was filtered rather than decanted in order to prevent any of the fine particles of meal, difficult at times to pack, from passing into the ex-

[6] R. A. Gortner, W. F. Hoffman and W. B. Sinclair, *Cereal Chem.*, **6**, 1 (1928); "Colloid Symposium Monograph," The Chemical Catalog Co., Inc., New York, **1928**, Vol. V, p. 179.

[7] E. V. Staker and R. A. Gortner, *J. Phys. Chem.*, **35**, 1565 (1931).

[8] Felix Saunders, THIS JOURNAL, **53**, 696 (1931).

[9] We are greatly indebted to the California Fruit Growers' Exchange for the seeds used in this study.

tract. Three extractions were carried out by the method described and the filtrates were combined. The Kjeldahl–Gunning method was used to determine the nitrogen in the combined filtrates. At least four determinations were run with each salt. Blanks were run on the salt solutions.

**Experimental.**—The experimental results are shown in Table I.

TABLE I

SOLUTION OF THE PROTEIN OF ORANGE SEEDS BY SODIUM SALTS

| Salt | Mg. of N from 6 g. of meal | % of total N extracted |
|---|---|---|
| Sodium chloride | 106 | 53.5 |
| Sodium bromide | 104 | 52.5 |
| Sodium iodide | 105 | 53.0 |
| Sodium bicarbonate | 104 | 52.5 |
| Sodium acetate | 102 | 51.5 |
| Sodium benzoate | 102 | 51.5 |
| Sodium salicylate | 101 | 51.0 |
| Sodium carbonate | 102 | 51.5 |
| Sodium sulfate | 106 | 53.5 |
| Sodium borate | 103 | 52.0 |
| Sodium tartrate | 103 | 52.0 |
| Disodium phosphate | 104 | 52.5 |
| Trisodium phosphate | 100 | 50.5 |
| Sodium citrate | 102 | 51.5 |
| Sodium dihydrogen phosphate | 81 | 40.9 |

The greatest discrepancy in this table is in the sodium dihydrogen phosphate extraction. The explanation probably lies in the fact that this was the only acid solution used and the presence of the acid might possibly have a denaturing effect on the protein. A compound such as a protean might be formed which would be less soluble in the salt solution than the original protein. In order to study further the effect of acid on pomelin, a mixture of equal parts of normal sodium chloride and normal hydrochloric acid was used as the extracting agent. As a result it was found that only about one-half as much nitrogen was obtained as would be expected. This gave more conclusive evidence that the presence of acid decreases the amount of nitrogen extracted. The slight variation observed for the other salts in the amount of nitrogen extracted might easily be considered within the range of experimental error.

## Discussion

The experimental data show that not only are the alkali halides alike in their ability to extract this protein, but that this property is characteristic of many other salts as well. It is of particular interest to observe that the globulin is uniformly soluble in salts of a strong base and weak acids as well as in neutral salts. Previous definitions of globulins have stated only that they are soluble in salts of strong bases and strong acids. The fact

that the salts are alkaline does not seem to decrease the amount of protein extracted as in the case of acid salts. The uniformity of the results obtained leads one to believe that a definite globulin is being extracted.

As stated before, this set of extractions shows no lyotropic series, indicating that the various anions are alike in their solvent effect upon the globulin. This evidence does not agree with that obtained by Gortner[6] in his studies on wheat and other seed proteins. However, in most cases he was probably working with a mixture of substances and might easily be extracting other substances with the globulin. This would account for the conflicting results. On the basis of these results he has raised an objection to the present definitions of globulins, which is justified by his experiments. Different salts may show a difference in their "peptizing" ability toward certain protein systems. In the case of orange seeds, however, uniformity seems to be the rule. Further studies along these lines are in progress.

## Conclusions

1. Normal solutions of the salts used in this study extract the same amount of nitrogen from the orange seed meal and there is no evidence for the existence of a lyotropic series in this particular system.
2. Pomelin is soluble equally as well in normal solutions of salts of strong bases and weak acids as in solutions of neutral salts.
3. The presence of acid during the extraction apparently decreases the amount of nitrogen extracted.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# SOME REARRANGEMENT REACTIONS OF BENZYLMAGNESIUM CHLORIDE

BY HENRY GILMAN AND JAMES E. KIRBY

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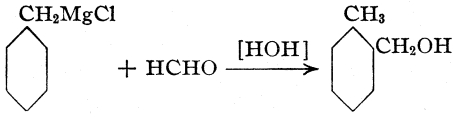
## Introduction

Organomagnesium halides are very widely used in studies of the mechanisms of organic reactions and in the proof of structure of compounds. Such utility would be markedly circumscribed by uncertainties concerning rearrangements of the Grignard reagents. The present study is a continuation of earlier work[1] on the mechanism of such rearrangements and a classification of reactants which induce such transformations, primarily with a view to learning which simple compounds might be used with confidence in studies of Grignard reagents.

[1] (a) Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927), and (b) Gilman and Kirby, *ibid.*, **51**, 3475 (1929).

The first reported rearrangement of this kind was in the reaction between benzylmagnesium chloride and formaldehyde as a consequence of which *o*-tolylcarbinol was formed.[2]




(I)

A second anomalous behavior of benzylmagnesium chloride was subsequently observed in its reaction with benzaldehyde,[3] and the course of this reaction is still not definitely known.[4] The related triphenylmethylmagnesium chloride, $(C_6H_5)_3CMgCl$, was also shown to react abnormally with benzaldehyde.[5] Such rearrangements, with a limited group of reactants, appear to be general with RMgX compounds having the grouping $-\overset{|}{C}=\overset{|}{C}-CH_2MgX$, if one may generalize from the behavior of $\alpha$-naphthylmethylmagnesium chloride,[1b] $\alpha$-$C_{10}H_7CH_2MgCl$; benzohydrylmagnesium chloride,[6] $(C_6H_5)_2CHMgCl$; and cinnamylmagnesium chloride,[1a,7] $C_6H_5CH=CHCH_2MgCl$.

The reactants which have been reported as undergoing abnormal transformations with this type of Grignard reagent are very few in number. Confining attention to benzylmagnesium chloride, anomalous behavior has been observed not only with formaldehyde and benzaldehyde and derivatives, but also with ethyl chlorocarbonate[8] and chloromethyl methyl ether.[9] From the present study it appears that the rearrangements with benzylmagnesium chloride are more general than has been suspected and include such compounds as ethylene oxide, ethyl formate, chloromethyl ethyl ether and acetyl chloride.

Of equal importance is the observation that the rearrangement does not involve exclusively the *ortho* position. For example, the reaction

[2] Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903); Grignard, *Bull. soc. chim.*, **29**, 953 (1903). $\beta$-Phenylethyl alcohol is not obtained in this reaction. (See p. 3542 of Ref. 7 of this paper.)

[3] Chichibabin, *Ber.*, **42**, 3474 (1909).

[4] Schmidlin and Banùs, *ibid.*, **45**, 3193 (1912); Marshall, *J. Chem. Soc.*, **105**, 527 (1914); **107**, 509 (1915); Banùs and Vila, *Anales. soc. españ. fís. quím.*, **19**, 326 (1921); [*Chem. Abstracts*, **16**, 3479 (1922)]; Banùs, *ibid.*, **26**, 372 (1928); [*Chem. Abstracts*, **23**, 2178 (1929)]; Banùs and Calvet, *ibid.*, **27**, 49 (1929); [*Chem. Abstracts*, **23**, 3205 (1929)].

[5] Schmidlin, *Ber.*, **39**, 4183 (1906); **41**, 426 (1908); Chichibabin, *ibid.*, **40**, 3965 (1907); Schmidlin and Hodgson, *ibid.*, **41**, 430 (1908). See, also, Gilman and Jones, THIS JOURNAL, **51**, 2840 (1929).

[6] Unpublished observations.

[7] Gilman and Harris, THIS JOURNAL, **53**, 3541 (1931).

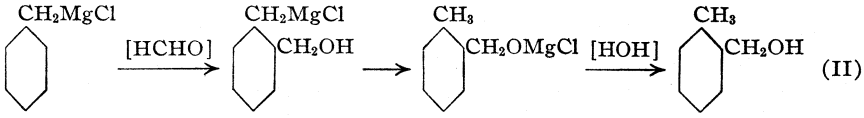
[8] See p. 1826 of Ref. 1a.

[9] Baeyer, German patent 154,658 [*Chem. Zentr.*, II, 1355 (1904)]. Bottomley, Lapworth and Walton, *J. Chem. Soc.*, 2215 (1930).

with ethylene oxide is the first clearly defined case of a para rearrangement, to the apparent exclusion of any ortho compound.[10] Chloromethyl ethyl ether and chloromethyl methyl ether[9] give both ortho and para rearrangement products. Ethyl formate likewise gives both types of rearrangement product, but the extent of para rearrangement is comparatively small. In brief, then, the rearrangements with benzylmagnesium chloride can be exclusively ortho or exclusively para or mixtures of the two in varying proportions depending on the reactants and the experimental conditions.

Not all reactants give rise to rearrangement products. It has been definitely shown that carbon dioxide gives exclusively the normal and expected phenylacetic acid, $C_6H_5CH_2COOH$. This is fortunate, in a sense, because the carbonation of Grignard reagents has been extensively employed for the characterization of such reagents. However, even this orthodox reagent is not reliable with *all* RMgX compounds inasmuch as it has been shown recently[1a,7] to react abnormally with the Grignard reagent prepared from cinnamyl chloride to give phenylvinylacetic acid, $C_6H_5C(COOH)HCH{=}CH_2$, and not phenylisocrotonic acid, $C_6H_5CH{=}CHCH_2COOH$. At present, therefore, it is impossible to select any reagent with definite assurance that it will undergo a so-called normal transformation with *all* types of Grignard reagents. There may or may not be such a reactant and only future experiments by a group of workers will answer the need. Not much is now known concerning RMgX compounds having the general grouping $-\overset{|}{C}{=}\overset{|}{C}-\overset{|}{C}-MgX$ because many of them, like $\alpha$-naphthylmethylmagnesium chloride,[1b] cinnamylmagnesium chloride,[11] allylmagnesium bromide[12] and *p*-methoxybenzylmagnesium bromide[13] have only recently become available, either at all or in satisfactory yields.

Several mechanisms have been proposed for the rearrangements of benzylmagnesium chloride. The first of these by Tiffeneau and Delange[2] involves the following sequence of reactions:




(II)

Then Schmidlin and Banùs[4] suggested that benzylmagnesium chloride might be an equilibrium mixture of benzenoid and quinonoid forms, in

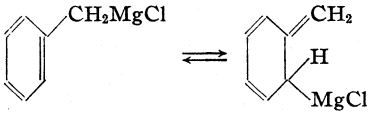
[10] Chichibabin[3] reported *p*-benzoylbenzoic acid among the oxidation products of the reaction between benzylmagnesium chloride and benzaldehyde. However, Schmidlin and Banùs, *Ber.*, **45**, 3193 (1912), failed to obtain that compound. A *para* rearrangement has been reported with triphenylmethylmagnesium chloride.

[11] Gilman and Harris, *Rec. trav. chim.*, **50** (1931).

[12] Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

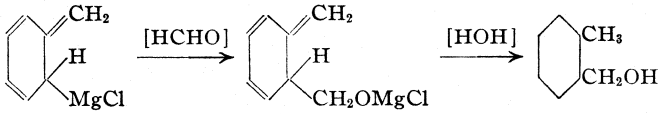
[13] Gilman and Zoellner, *ibid.*, **49**, 7 (1931).

accordance with the two corresponding forms suggested for the related triphenylmethylmagnesium chloride:




(III)

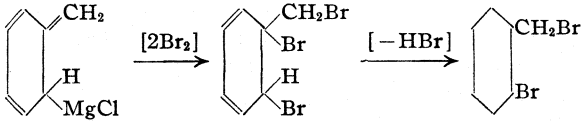
With this mechanism, the equilibrium is shifted completely to the left with carbon dioxide, to the right with formaldehyde, and with benzaldehyde the displacement of the equilibrium depends on the concentration of reactants and the mode or order of addition of the Grignard solution. At that time there was no observed para rearrangement with benzylmagnesium chloride. However, our present para rearrangement (with ethylene oxide, for example) can be fitted in with such a scheme of things by merely introducing a para-quinonoid form; and, where both ortho and para rearrangements are observed, it only becomes necessary to extend equilibrium (III) to include the para-quinonoid form. Using formaldehyde as a type, the quinonoid form is believed to react as follows[4]




(IV)

Banùs and Vila[4] are inclined to discard the quinonoid form (III) because one molecule of it should react with one molecule of a di-carbonyl compound like benzil and because *o*-tolylmagnesium halides react normally with benzaldehyde.[14]

The quinonoid form might be expected to react with bromine to some extent at low temperatures to give *o*-bromobenzyl bromide, as follows



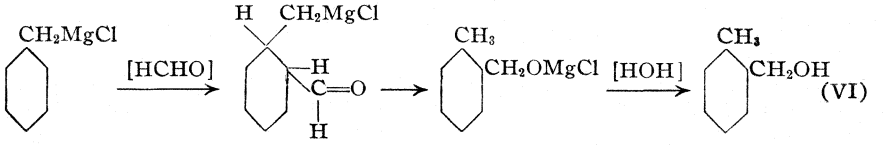

(V)

The only product isolated from this reaction was benzyl bromide of high purity. This experiment is hardly of unequivocal importance, because the equilibrium (III) might have been shifted under the experimental conditions. The presence of a quinonoid form might be definitely ascertained by chemical means were it possible to reduce catalytically benzylmagnesium chloride, which so far is not the case. Catalytic reduction followed by carbonation and hydrolysis would be expected to give among the products 2-methylcyclohexanecarboxylic acid. Ozonization, likewise, is of little

[14] Banùs and Medrano, *Anales soc. españ. fís. quím.*, **21**, 436 (1923); [*Chem. Abstracts*, **18**, 2144 (1924)]. They point out that the normal reaction with *o*-tolylmagnesium halides implies that it is not in equilibrium with the quinonoid form of benzylmagnesium chloride, (III).

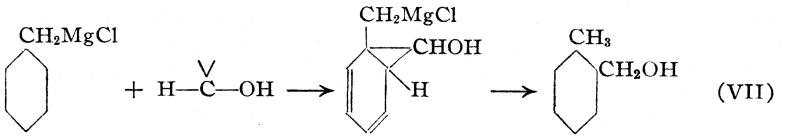
present promise, but for another reason: namely, the highly explosive reaction between phenylmagnesium bromide and ozone.[15] Absorption spectra studies now in progress with triphenylmethylmagnesium halides may be of assistance.

Other mechanisms, using formaldehyde as the reactant, are the following[16]



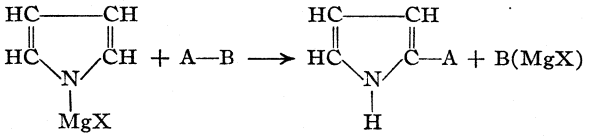

(VI)

and that involving a methylenic modification of formaldehyde




(VII)

Admittedly, none of the several proposed interpretations has any convincing experimental support. If the latter interpretations and that of Tiffeneau and Delange[2] have any merit, it lies in the emphasis they direct to the fact that no migration of the —MgX has necessarily occurred and the apparent rearrangement is one that ensues when the RMgX compound reacts with particular compounds. This is well illustrated with pyrrylmagnesium halides where the —MgX group is almost certainly attached to nitrogen and yet in many reactions the substituent finds itself generally on the $\alpha$-carbon atom.[17]



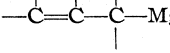

(VIII)

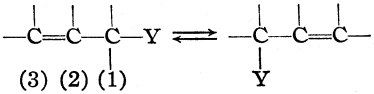
Whatever explanation may be correct, it appears to be definitely established that the rearrangement reactions of benzylmagnesium chloride types are general with RMgX compounds having the grouping: —C=C—C—MgX. It apparently does not occur with cyclohexylmethylmagnesium halides, $C_6H_{11}CH_2MgX$; and our experiments have shown that there is no nuclear rearrangement with formaldehyde and $\beta$-phenylethylmagnesium bromide, $C_6H_5CH_2CH_2MgBr$, $\beta$-styrylmagnesium bromide, $C_6H_5CH{=}CHMgBr$, and phenylacetenylmagnesium bromide, $C_6H_5C{\equiv}CMgBr$. It would be interesting to ascertain whether *o,o,p*-trisubstituted benzylmagnesium halides undergo rearrangement.

[15] Private communication from Professor L. I. Smith.

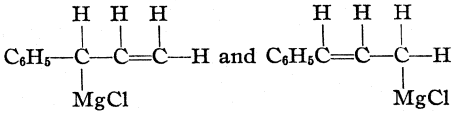
[16] J. E. Kirby, Doctoral Thesis, Iowa State College, 1929.

[17] Gilman and Heck, THIS JOURNAL, **52**, 4949 (1930).

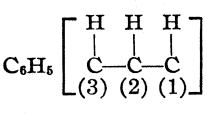
Inasmuch as the rearrangement is common to compounds having the  group, it appears altogether reasonable to consider them as allylic rearrangements

 (IX)

of a three-carbon system where the element or group (Y) shifts from carbon (1) to carbon (3) with the accompanying displacement of a double bond. Such an interpretation has very recently[7] been proposed for cinnamylmagnesium chloride reactions. Despite the fact that there is no general agreement on the mechanism or mechanisms underlying allylic rearrangements, the case for cinnamylmagnesium chloride finds support with related types. With cinnamylmagnesium chloride we have the following

 (X)

and all reactions so far studied are best explained on the basis of the first formula. The second formula is not excluded because, as with pyrrylmagnesium halides, the position of the —MgX group need not be that assumed by the group which replaces it. The two formulas illustrated in (X) may be merged and represented by the internally symmetrical formula given (with the MgX ion or ions held electrostatically) and from an electronic viewpoint the difference in electron attraction between a phenyl group and the hydrogen displaces the electrons in the brackets from right to left and so determines whether the entering group or element attaches itself to carbon (1) or carbon (3). Such a scheme adapts itself to some of the cinnamyl derivatives. For example, carbon (3) being relatively negative would attract and hold the —MgX group, and carbon (1) being relatively positive would attract a halogen.



In the case of benzylmagnesium chloride and related aryl-$CH_2MgX$ types, the double bond necessary for an allylic system is contained in the benzene nucleus. This, however, need not affect seriously such a system because it has been definitely shown that such nuclear unsaturation gives normal conjugated system reactions with RMgX compounds when the nuclear olefinic linkage is conjugated with lateral unsaturation as in benzophenone-anil,[18] $(C_6H_5)_2C{=}NC_6H_5$, and highly phenylated ketones.[19] If we admit an allylic system for the rearrangements of benzylmagnesium

[18] Gilman, Kirby and Kinney, THIS JOURNAL, **51**, 2252 (1929).

[19] Kohler and Nygaard, *ibid.*, **52**, 4128 (1930).

chloride, we are thrown back to the quinonoid form (III) of Schmidlin and Banùs[4] as one of several explanations of allylic rearrangements. However, not only is there no present agreement on the mechanism of allylic rearrangements in general, but there are explanations which interpret the "rearrangement" without recourse to the migration of elements or groups.[7] Furthermore, an extension of allylic systems is desirable to include para rearrangements. It is interesting to recall that with cinnamylmagnesium chloride[7] the rearrangement is apparently halted in the lateral allylic system and that no so-called double-allylic rearrangement occurs to give an ortho or para nuclear substituted product. This need not be interpreted to mean that there is no allylic system in the benzylmagnesium chloride type which results, namely, $\begin{matrix} C_6H_5C{-}CH{=}CH_2 \\ | \\ MgCl \end{matrix}$. Instead, there is the possibility that the $C_6H_5CH{=}CHCH_2MgCl$ underwent one allylic rearrangement with a given reactant, and that the formation of the product (with carbon dioxide, $C_6H_5CH(COOH){-}CH{=}CH_2$) destroyed the —MgX group and so rendered impossible a second allylic rearrangement to the nucleus. Because of a similarity between cinnamylmagnesium and benzylmagnesium halides, it is reasonable to assume that the rearrangements of benzylmagnesium halide types also involve free radicals[7] and the electronic interpretations which have been proposed for general allylic rearrangements.[7]

## Experimental Part

**Oxidation Procedure for Nuclear Substitution Products.**—Because of the difficulty in isolating small quantities of reaction products, the residual oils and in some cases all of the product, were oxidized to the corresponding acids and any benzoic, phthalic and terephthalic acids identified by customary methods. In general, an excess of permanganate was employed, usually in concentrations of about 5% and containing about 10% of sodium or potassium hydroxide. At the conclusion of the oxidation, which required from thirty minutes to several hours, depending on the nature of the material, the excess permanganate was destroyed by adding a little alcohol, and the heavy manganese dioxide precipitate filtered off with suction. After washing the sludge of manganese dioxide with a little dilute alkali, the filtrate and washings were combined and acidified with hydrochloric acid.

The separation depends on the varying solubilities of benzoic, phthalic and terephthalic acids in water and chloroform. Benzoic acid is soluble in water[20] to the extent of 0.34 g. in 100 g. at 25°, and soluble in chloroform; phthalic acid is soluble in water[21] to the extent of 0.54 g. in 100 g. at 14°, and insoluble in chloroform;[22] and terephthalic acid is only soluble in water[23] to the extent of one part in 67,000, and insoluble in chloroform.[23]

On acidification, all of the terephthalic acid precipitates along with part of the benzoic acid, which is usually present in the largest quantity. The phthalic acid stays in solution along with the remainder of the benzoic acid. The precipitated acids are

[20] Hoffmann and Langbeck, *Z. physik. Chem.*, **51**, 394 (1905).

[21] Graebe, *Ann.*, **238**, 321 (1887).

[22] Zincke and Breuer, *ibid.*, **226**, 53 (1884).

[23] Baeyer, *ibid.*, **251**, 284 (1889).

separated by simply extracting the benzoic acid from the terephthalic acid with chloroform. The water solution is extracted two or three times with ether, the ether dried over sodium sulfate and evaporated to dryness. The residual benzoic acid and phthalic acids are separated by a chloroform extraction of the benzoic acid. Had isophthalic acid formed during any of the oxidations it would have escaped detection in the above procedure. The solubility of isophthalic acid in water is low (1 part in 7800) and it probably would have appeared along with the terephthalic acid.

**Carbon Dioxide.**—An ether solution of 0.5 mole of benzylmagnesium chloride was sprayed upon the vanes of a stirrer contained in a flask, cooled by an ice–salt mixture, through which carbon dioxide circulated. Despite the apparent purity of the resulting phenylacetic acid, it was fractionally crystallized in an unsuccessful effort to isolate any toluic acids which might be present. Hot water was used as the solvent because *o*- and *p*-toluic acids are less soluble than phenylacetic acid in water. Oxidation of the yellow residual oil gave only benzoic acid.

**Bromine.**—A cold solution of 0.25 mole of benzylmagnesium chloride was added over a one-half hour period to a 0.5 mole solution of bromine in ether cooled by carbon dioxide snow and ether. The cold mixture was immediately hydrolyzed by pouring upon cracked ice. Practically all of the product distilled at 73–74° (10 mm.) to give a 63% yield of benzyl bromide, which was characterized as benzyl phthalimide.

**Benzonitrile.**—The yield of phenyl benzyl ketone from a 0.3 mole run was 53.4%. The ketone was identified by a mixed melting point determination with an authentic specimen, and by its oxime. Because of difficulty with the nitric acid oxidation[24] of phenylbenzylcarbinol, $C_6H_5CHOHCH_2C_6H_5$, to the ketone, 10 g. of the carbinol was oxidized by stirring for one hour at 50–60° with a solution containing 4.5 g. of sodium dichromate and 6 cc. of concentrated sulfuric acid in 100 cc. of water.

Exhaustive permanganate oxidation of the oily residue from the Grignard reaction gave only benzoic acid.

**Chloroacetophenone, $C_6H_5COCH_2Cl$.**—Oxidation of the mixture from a low temperature (−18°) reaction between 0.1 mole of chloroacetophenone and 0.7 mole of benzylmagnesium chloride gave only benzoic acid.

**Diphenylcarbamine Chloride, $(C_6H_5)_2NCOCl$.**—The acid amide mixture from a 0.1-mole run of diphenylcarbamine chloride and benzylmagnesium chloride was hydrolyzed by alcoholic potash to give phenylacetic acid but no toluic acids.

**Acetyl Chloride.**—*o*-Methylacetophenone and related products are formed to a limited extent, because oxidation of the reaction mixture from acetyl chloride and benzylmagnesium chloride gave not only benzoic acid but also a very small quantity of phthalic acid.

**Ethylene Oxide.**—Ethylene oxide was distilled into a 0.5 mole solution of benzylmagnesium chloride until a negative color test[25] showed that the Grignard reagent had been used up. The thick mixture was broken up, toluene added, most of the ether distilled off, and the mixture then refluxed with stirring for one hour. After hydrolysis, the mixture was steam distilled. An ether extraction of the steam distillate gave 32.5 g. or 47.8% of a colorless oil with fragrant odor, distilling at 113–115° (10 mm.).

The non-volatile residue from the steam distillation yielded a small amount of terephthalic acid on oxidation.

Oxidation of a 4-g. sample of the oil obtained as a major reaction product gave 1 g. of benzoic acid and nearly 1 g. of terephthalic acid. No phthalic acid was isolated. The oil, which liberates gas with sodium, appears to be a mixture of γ-phenylpropanol and one or more of its isomers.

[24] Limpricht and Schwanert, *Ann.*, **155**, 64 (1870).

[25] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

**Chloromethyl Ethyl Ether,** $ClCH_2OC_2H_5$.—Several experiments were carried out with the chloro ether prepared in accordance with the directions of Wedekind.[26] Oxidation of the products from one run gave benzoic, phthalic and terephthalic acids in quantities which showed that approximately 53% of the reaction was normal, 16% ortho rearrangement and 31% para rearrangement.

From another experiment in which 0.3 mole of the chloro ether was added to an equivalent quantity of the cooled benzylmagnesium chloride, there was obtained 21.9 g. of an oil distilling at 93–97° (7 mm.) and an indefinite oil collected over 170–220° (7 mm.). Permanganate oxidation of a 5.01-g. sample of the low boiling oil gave 1.133 g. of benzoic acid, 0.655 g. of terephthalic acid and 0.092 g. of phthalic acid. The high boiling oil was redistilled and a middle fraction of 1.9 g. was taken between 165–180° (6 mm.), most of it coming over at 175°. Oxidation of this fraction gave 0.2 g. of benzoic acid, 0.1 g. of phthalic acid and 0.2 g. of terephthalic acid.

In a third experiment, carried out like the first by adding the Grignard reagent to the chloro ether, 28 g. of oil distilling at 93–97° (7 mm.) and 5.4 g. distilling between 130–220° (7 mm.) were obtained. Oxidation of 10.68 g. of the low boiling oil gave 3.934 g. of benzoic acid, 0.465 g. of phthalic acid and 1.75 g. of terephthalic acid. Zeisel analyses gave considerable difficulty in the way of obtaining satisfactory check values from aliquots of a selected batch of oil. Because of this difficulty, some ethyl $\beta$-phenylethyl ether, $C_2H_5OCH_2CH_2C_6H_5$, was synthesized in order to ascertain whether the trouble was inherent in an ether of this type, which is the normal reaction product of benzylmagnesium chloride and chloromethyl ethyl ether. The ethyl $\beta$-phenylethyl ether was finally synthesized as follows.

Eight grams (0.35 atom) of metallic sodium in thin slices was added to a solution of 36.6 g. (0.3 mole) of phenylethyl alcohol in dry benzene. The mixture was stirred mechanically and refluxed for about seventeen hours to insure as nearly complete conversion of the alcohol to alcoholate as possible. Fifty-five grams (0.36 mole) of ethyl sulfate was then added through the dropping funnel. A pasty mass separated. The mixture was stirred and refluxed for eight hours. The mass was then removed from the stirring flask and the small pieces of unused sodium removed. Strong ammonium hydroxide was then added and the mixture warmed to hydrolyze the excess ethyl sulfate. The whole mixture was then steam distilled. The oil collected was washed three times with water, then with 50% calcium chloride solution, and finally dried over anhydrous calcium chloride. The benzene was then distilled off and the residual oil distilled under reduced pressure. The yield of oil boiling at 77–82° (7 mm.) was 25.8 g., corresponding to 57.3% of the theoretical amount. On redistillation the boiling point was found to be 85–87° (7 mm.); $d_{25}^{25}$ 0.9200; $n_D^{25}$ 1.4708. A Zerewitinoff analysis of this oil showed no active hydrogen. Although one Zeisel analysis gave a correct value, several were about 2% low.

**Ethyl Chlorocarbonate,** $ClCOOC_2H_5$.—A solution of 0.25 mole of benzylmagnesium chloride was prepared in the usual manner from 32 g. of benzyl chloride and 6.1 g. of magnesium turnings. The Grignard solution was quickly filtered through glass wool into a separatory funnel. A solution of 126 g. (1.0 mole) of ethyl chlorocarbonate in twice its volume of anhydrous ether was placed in a one-liter 3-necked flask and cooled in an ice–salt mixture. The Grignard solution was then slowly added to the solution in the flask. The addition required about forty-five minutes, vigorous stirring being maintained during the addition. After hydrolyzing with iced hydrochloric acid, the whole mixture was steam-distilled. The distillate was extracted with ether, the ether extracts dried over sodium sulfate and the ether then distilled off. The remaining oil was

[26] Wedekind, *Ber.*, **36**, 1383 (1903). From our experiments we recommend that the chloromethyl ethyl ether be fractionated under reduced pressure.

refluxed for three hours with 10% alcoholic potassium hydroxide. The solution was cooled, extracted with ether to remove unhydrolyzed oils, and then acidified with hydrochloric acid. The total volume was then about 800 cc. The solution was milky but contained no crystals. After about two hours a few flaky crystals separated and were filtered off. These weighed 1.0 g. (2.9%) and melted at 103–105°. A mixed melting point with *o*-toluic acid was found to be 103°. The remaining water solution was twice extracted with ether, the ether extracts washed with a little cold water and in turn extracted with 100 cc. of 10% potassium hydroxide. On acidification with hydrochloric acid and cooling, 4.7 g. of slightly impure phenylacetic acid was obtained in the form of shining leaflets melting at 68°. A mixed melting point with phenylacetic acid was 71°. This fractional separation of *o*-toluic and phenylacetic acids was of course not quantitative. Approximately 20% of ortho rearrangement appears to have occurred.

A second experiment was carried out in the hope of showing the presence of ethyl *p*-toluate in the reaction products along with ethyl phenylacetate and ethyl *o*-toluate. Two-tenths mole of benzylmagnesium chloride solution was slowly added to a well-stirred solution of 40 g. (0.37 mole) of ethyl chlorocarbonate in 200 cc. of ether. The temperature was kept at about −13–15° by means of an ice–salt mixture. The addition required about one hour. A color test showed the absence of Grignard reagent. After hydrolyzing with ice and dilute hydrochloric acid, the mixture was steam-distilled until nothing more came over. The residual tar was exhaustively oxidized in the customary manner. A trace of *o*-phthalic acid was found and a cloudiness indicative of terephthalic acid.

The oil and ether from the steam distillation were separated from the water and dried over sodium sulfate. The ether was distilled off and the temperature raised to 110° to remove unused ethyl chlorocarbonate. The residue yielded 9.5 g. of liquid esters boiling at 98° (6 mm.). This corresponds to a yield of 29% of mixed, isomeric esters. The total amount of oil was hydrolyzed by refluxing for six hours with 10% alcoholic potash. Acidification yielded an oily precipitate and attempts to crystallize from water were fruitless. The oil was recovered from the water by ether extraction, and then taken up in 95% alcohol and set aside to crystallize slowly. After about three months a crop of heavy, blunt needles, many over one-half inch long, had formed. These needles were removed from the oil and dried on filter paper; yield, 1.1 g.; m. p. 100–101°. A mixed melting point determination showed them to be *o*-toluic acid. The residual oil weighed 4.0 g. The yield of *o*-toluic acid was 4% based on Grignard reagent used; 14% based on the total ester obtained; and 21.5% on the total acid derived by hydrolysis of the ester.

**Ethyl Formate.**—Oxidation of the reaction mixture obtained by adding 0.3 mole of benzylmagnesium chloride to 0.3 mole of ethyl formate at −18°, yielded 9 g. of benzoic acid, 0.75 g. of phthalic acid and a quantity of terephthalic acid insufficient to isolate.

**Benzyl Chloride.**—A mixture of 0.2 mole of benzylmagnesium chloride and 0.2 mole of benzyl chloride was refluxed for two and one-half hours after stirring for three hours at room temperature. A negative color test showed that the Grignard reagent had been used up. The yield of dibenzyl was 64.8%. Exhaustive oxidation of the oils gave only benzoic acid.

**Cyclohexylmethylmagnesium Bromide ($C_6H_{11}CH_2MgBr$) and Formaldehyde.**—Gaseous formaldehyde was added to 0.25 mole of cyclohexylmethylmagnesium bromide[27] until a negative color test was obtained (forty-five minutes). The yield of cyclohexyl-

[27] There was no difficulty in initiating the formation of this Grignard reagent, which, incidentally, was completely free of any color or cloudiness.

ethanol[28] was 14.7 g. or 46%; b. p. 198–202° (742 mm.); $n_D^{26}$ 1.4648. The oil was identified by oxidation to β-cyclohexylacetaldehyde.[28] The semicarbazone of the aldehyde, after recrystallization from alcohol, melted at 147–149°,[29] and the cyclohexylacetamide (m. p., 165–166°) showed no depression in a mixed melting point determination. The identification of by-products has not been completed.

**Formaldehyde with β-Phenylethylmagnesium Bromide** ($C_6H_5CH_2CH_2MgBr$), **β-Styrylmagnesium Bromide** ($C_6H_5CH{=}CHMgBr$) **and Phenylacetenylmagnesium Bromide** ($C_6H_5C{\equiv}CMgBr$).—Formaldehyde was passed into each of these three Grignard reagents until a negative color test was obtained. Oxidation of parts of the main reaction products and of residual oils gave only benzoic acid.

**Sodium Phenate and Ethyl Chlorocarbonate.**—In order to determine whether sodium phenate, $C_6H_5ONa$, might undergo nuclear substitution by rearrangement under the moderate conditions used with benzylmagnesium chloride, 0.3 mole of ethyl chlorocarbonate was added slowly with vigorous stirring to 0.3 mole of sodium phenate in toluene at −18°. The initial heavy paste disappeared, and after allowing the mixture to warm up to room temperature it was hydrolyzed. The yield of ethyl phenylcarbonate was 28.2 g. or 56.6%. No ethyl salicylate (one of the possible rearrangement products) was isolated.

## Summary

Benzylmagnesium chloride undergoes rearrangement reactions with a variety of compounds. The rearrangement may be exclusively ortho, exclusively para or mixtures of ortho and para in varying proportions depending on the reactants and on experimental conditions. Carbon dioxide and some other reagents behave normally. The rearrangements of benzylmagnesium chloride and related types having the group $-\overset{|}{C}{=}\overset{|}{C}-\overset{|}{C}-MgX$ can be correlated with allylic or three-carbon system rearrangements.

AMES, IOWA

[28] Hiers and Adams, THIS JOURNAL, **48**, 1091 (1926).

[29] Wallach, *Ann.*, **359**, 313 (1908), reported that m. p. as 132–134°. Zelinsky, *Ber.*, **41**, 2628 (1908) prepared the ethanol and his constants are in agreement with ours. The melting point of the semicarbazone of the aldehyde was not given in the *Ber.* reference. See, also, Zelinsky, *J. Russ. Phys.-Chem. Soc.*, **38**, 930 (1906).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

# A POSSIBLE SOURCE OF ERROR IN DETERMINING THE CONSTITUTION OF DI- AND POLYSACCHARIDES

BY JAMES COLQUHOUN IRVINE AND RICHARD PATRICK MCGLYNN

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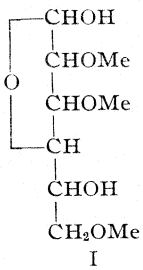
The results contained in the present communication confirm the idea expressed in former papers that the isolation of crystalline 2,3,6-trimethylglucose (m. p. 121°) from the hydrolysis products of a methylated carbohydrate does not provide decisive evidence as to the constitution of the parent compound. The evidence is, in fact, ambiguous as the compound under examination may equally be a derivative of normal glucose or of γ-glucose. This conclusion, which affects profoundly many investigations on the structure of disaccharides and of polysaccharides based upon glucose, creates a position which was not unforeseen by us.

From the time that Irvine and Black[1] proved that maltose gives the same methylated sugars as does cellobiose, it has been evident that it is insufficient merely to identify the sugars formed on hydrolyzing a methylated disaccharide and to determine the structure of these scission products. There remains another factor of equal importance, as proof must be forthcoming that the methylated hexoses isolated actually contain the same oxygen-ring systems that were present in the initial disaccharide. Unless this condition is fulfilled the conclusions drawn from the results of methylation may be misleading. This point was emphasized by one of us several years ago[2] in discussing the constitution of glucosediacetone but its importance has been frequently overlooked by other investigators.

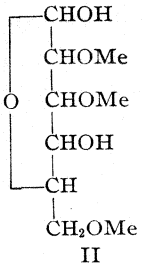
In most constitutional studies of disaccharides by the method now under discussion, a trimethyl and a tetramethyl hexose are formed, and in many cases the accepted structure of the parent sugar has been arrived at merely by attaching two hexose residues in the position best suited to accommodate the result. Of the methylated sugars which function as reference compounds in this type of research, greatest importance must be attached to 2,3,6-trimethylglucose, which has been isolated from such sugars as maltose, cellobiose and lactose, to quote only prominent examples. Now although certain sugars (*e. g.*, 2,3,4,6-tetramethylglucose) are incapable under ordinary conditions of undergoing any shift in the internal oxygen-ring, a circumstance which renders their isolation of decisive value in constitutional studies, the same assurance does not extend to the case of 2,3,6-trimethylglucose. As Irvine and Black pointed out, this sugar can exist in an unstable modification (Formula I), which has only a transient existence owing to its transformation into the stable form (Formula II), actually isolated.

[1] Irvine and Black, *J. Chem. Soc.*, **129**, 862 (1926).

[2] Irvine and Patterson, *ibid.*, **121**, 2149 (1922).



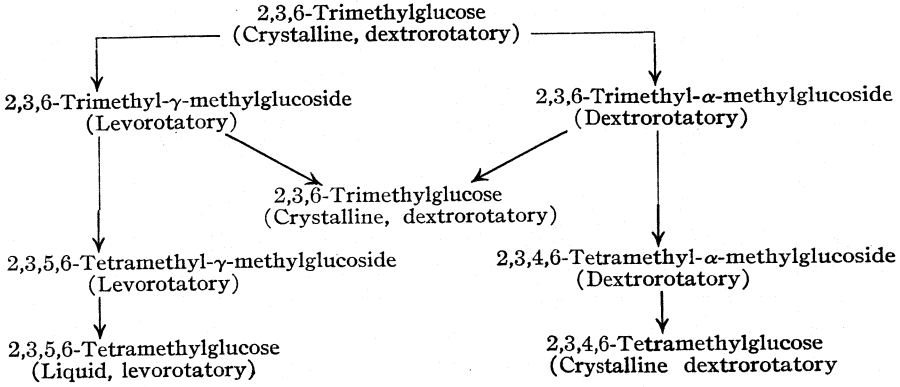

I



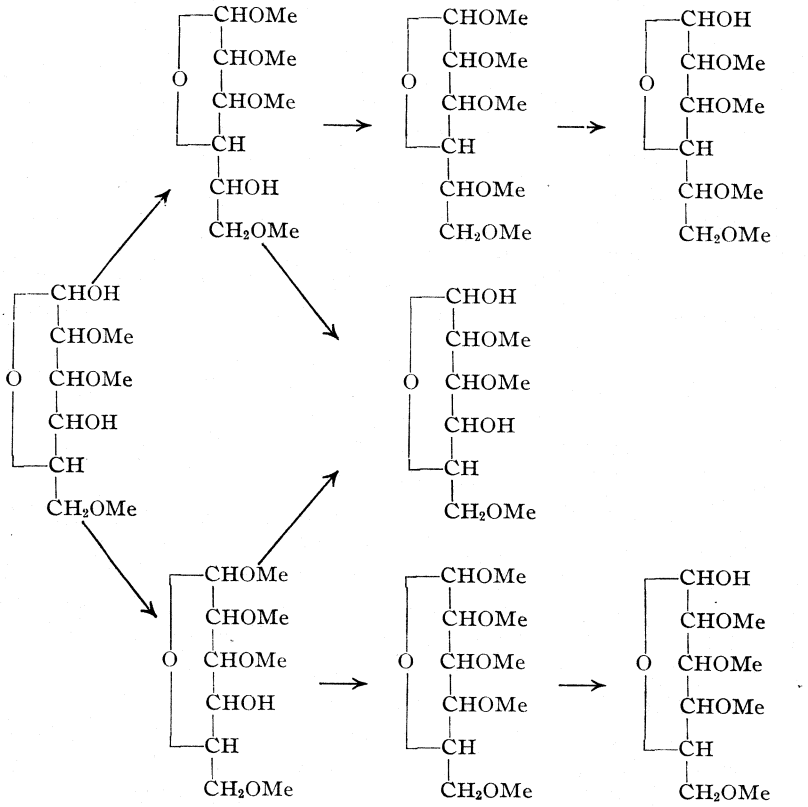

II

It follows that two distinct types of disaccharide containing, respectively, amylene oxide and butylene oxide rings in the reducing hexose residue (*e. g.*, glucose-5-glucoside and glucose-4-glucoside) would give precisely the same methylated sugars when the customary methods are applied and in order to ascertain if this view is valid we have examined a test case. We have converted 2,3,6-trimethylglucose into isomeric 2,3,6-trimethyl methylglucosides which differ only in the oxygen linkage present in each case. One of these compounds is definitely a $\gamma$-form (corresponding to Formula I) as it is convertible into 2,3,5,6-tetramethyl-$\gamma$-glucose, whilst the other belongs, equally definitely, to the normal type (corresponding to Formula II), as is shown by its transformation into 2,3,4,6-tetramethylglucose. Nevertheless these isomerides, when subjected to hydrolysis, gave crystalline 2,3,6-trimethylglucose as the only product. The result is convincing and shows that the isolation of the crystalline variety of 2,3,6-trimethylglucose in any structural investigation can be just as misleading as the isolation of levorotatory fructose by the hydrolysis of sucrose. The cases are analogous. It cannot be too frequently emphasized that the interconversion of a sugar into isomeric forms of the same sugar is not restricted to change in $\alpha$- or $\beta$-configuration of the reducing group, but includes in addition alteration in the position of the internal oxygen-ring where such a change is possible.

The scheme of this part of the research may be summarized as



When these results are expressed in terms of structural formulas the intramolecular changes involved may be followed.




The test case submitted above is sufficiently decisive to show that much further work and the application of new methods are alike necessary before definite constitutions can be assigned to the disaccharides and polysaccharides which are convertible into 2,3,6-trimethylglucose and, for the time being, an arbitrary choice should be made between the two alternative oxygen-ring systems present in starch and cellulose, respectively; it has been, in fact, the detailed study of these polysaccharides which has led to the revision of the structural formulas of the corresponding disaccharides.

The investigation has also revealed that the oxidation reactions of methylated sugars which are frequently employed in determining constitution are likewise invested with complications. In such reactions, precisely as in glucoside formation, the oxygen-ring of a methylated sugar or of its derivatives may alter from one position to another so that, for example, the starting material may be an amylene oxide and the final product a $\gamma$-lactone containing the butylene oxide ring. In fact, the oxidation

of one and the same substance may give rise under varying conditions to either γ- or δ-lactones, thus rendering the structural evidence ambiguous. One example may be quoted. Crystalline 2,3,6-trimethylglucose if oxidized with bromine water under conditions which permit of the accumulation of hydrogen bromide yields directly the γ-lactone of 2,3,6-trimethylgluconic acid as the main product. In sharp distinction, when the sugar is oxidized by the same reagent but in the absence of halogen acid, the δ-lactone is produced in preponderating amount. There is probably no reaction of a reducing sugar in which similar changes of the internal oxygen ring do not take place to some extent provided the necessary hydroxyl groups are unsubstituted and this possibility cannot with safety be overlooked.

This consideration raises the question of what factors are operative in converting sugars into their γ-forms. Once more selecting 2,3,6-trimethylglucose as a test case, we find that change of temperature has little or no effect in altering the amount of the γ-form present in solution. The customary experimental procedure in which the γ-derivatives of a sugar are prepared at low temperatures thus seems to be dictated by the instability of these compounds rather than by alteration of the equilibrium stable form $\rightleftarrows$ γ-form. On the other hand, the influence of halogen acid in converting a sugar into γ-forms is profound and we have shown that both hydrogen bromide and hydrogen chloride are particularly effective. Having engaged on this problem, we are now making a systematic survey of the conditions under which all types of sugars can react in γ-modifications and in the course of the work have examined cases where, on theoretical grounds, no such conversion is possible. One of these examples is furnished by 2,3,4,6-tetramethylglucose which, when dissolved in acid methyl alcohol under conditions favorable to the formation of a γ-glucoside, shows a steady diminution in dextro-rotation until the reducing action upon Fehling's solution vanishes. These results might be regarded as sufficient to indicate that the sugar was actually reacting in a γ-form, which it could do only by transference of a methoxyl group from one position to another. We find, however, that such is not the case and that the changes mentioned are due to the formation of the corresponding semi-acetal which readily breaks down to regenerate the parent sugar. The result is quoted as an additional example emphasizing the caution which must be exercised by workers in this field even when employing processes apparently well-defined and decisive.

## Experimental

**Preparation of 2,3,6-Trimethylglucose.**—Cotton cellulose was subjected to graded acetolysis according to the method described by Irvine and Robertson[3] and the amor-

[3] Irvine and Robertson, *J. Chem. Soc.*, **129**, 1488 (1926).

phous mixture of acetates thus obtained was methylated by the joint use of methyl sulfate and 60% sodium hydroxide, the product being isolated in the usual manner. Six methylations with 30% caustic soda were necessary in order to raise the methoxyl content to 45.8%. In this way a mixture of trimethyl dextrins was obtained in the form of a yellow viscous sirup which weighed, on an average, 50% of the cellulose originally taken. The process is convenient, provided the conditions of acetolysis have been determined for the particular form of cellulose employed.

The sirup was then hydrolyzed by boiling with 8% hydrochloric acid for thirty minutes and the liberated sugar was thereafter isolated and purified in the usual manner. The yield of crystalline product, showing m. p. 121° and $[\alpha]_D$ +70.9°, amounted to 40% of the methylated sirup from which it was prepared.

**Conversion into 2,3,6-Trimethyl-γ-methylglucoside.**—The following is an account of one typical preparation. The sugar (10 g.) was dissolved in a liter of methyl alcohol containing 0.3% of hydrogen chloride and the solution was maintained at the temperature of the room, samples being abstracted at intervals in order to determine changes in specific rotation and in the reaction toward Fehling's solution. After remaining constant for an initial period, the optical activity diminished regularly and ultimately became levo, a constant value being observed when the reaction had proceeded for one hundred hours. At this stage the product behaved like a glucoside toward Fehling's solution. On plotting specific rotations against time a smooth curve was obtained and only significant figures are therefore quoted.

| Time | $[\alpha]_D$ | Time | $[\alpha]_D$ |
|---|---|---|---|
| 3 Minutes | +70.5° | 39 Hours | + 7.1° |
| 10 Minutes | +70.5 | 72 Hours | −14.0 |
| 45 Minutes | +70.5 | 88 Hours | −17.4 |
| 15 Hours | +32.5 | 100 Hours | −23.5 |

It may be mentioned that the same condensation has already been carried out on a small scale by Denham and Woodhouse[4] and by Irvine and Hirst.[5] These observers obtained, however, a different end-point, *viz.*, $[\alpha]_D$ −33 and −36°, respectively, the increased levorotation being due in all probability to the slow formation of secondary products. After neutralizing with silver carbonate and removal of the solvent, the residual sirup was dissolved in water and extracted with chloroform in order to free the glucoside from traces of unchanged sugar. On evaporation of the solvent, trimethyl-γ-methylglucoside remained as a sirup which was purified by distillation at low pressures. The yield was nearly quantitative (b. p. 180° (0.05 mm.); OMe, 51.8%; $n_D^{17}$ 1.4581; $[\alpha]_D$ in water −26.3° for $c$ = 1.20).

*Anal.* Calcd. for $C_{10}H_{20}O_6$: C, 50.85; H, 8.47. Found: C, 50.79; H, 8.44.

**Proof that the Above Glucoside Belongs to the γ-Series.**—The specific rotation of the compound and its instability to dilute acid might be accepted as sufficient evidence that the form of trimethyl methylglucoside described above is a derivative of γ-glucose, but it was considered advisable to confirm this point by conversion into tetramethyl-γ-methylglucoside. The glucoside was accordingly subjected to two successive treatments with silver oxide and methyl iodide, the product being isolated in the usual manner and purified by distillation (b. p. 115° (0.35 mm.)). The clear sirup thus obtained gave the correct analytical figures and was identical with the tetramethyl-γ-methyl-glucoside first described by Irvine, Fyfe and Hogg.[6]

[4] Denham and Woodhouse, *J. Chem. Soc.*, **111**, 249 (1917).

[5] Irvine and Hirst, *ibid.*, **121**, 1213 (1922).

[6] Irvine, Fyfe and Hogg, *ibid.*, **107**, 524 (1915).

| | Found | Quoted by Irvine, Fyfe and Hogg |
|---|---|---|
| $n_D^{15}$ | 1.4454 | 1.4458 |
| $[\alpha]_D$ in water | −16.0° | −14.6° |
| B. p., °C. | 115 (0.35 mm.) | 106 (0.25 mm.) |
| OMe | 61 | 61 (Calcd. 62%) |

In order to obtain an additional proof the tetramethyl-γ-methylglucoside was hydrolyzed by heating at 100° with *N*/100 hydrochloric acid. The action was followed polarimetrically, the curve of the optical changes being identical with that plotted from the results of Irvine, Fyfe and Hogg for the hydrolysis of their original preparation of tetramethyl-γ-methylglucoside. The highly characteristic change in which the specific rotation first increased to a maximum negative value and then decreased to a constant was duly observed.

| Time of heating | $[\alpha]_D$ | Time of heating | $[\alpha]_D$ |
|---|---|---|---|
| 0 | −11.1° | 90 Minutes | −19.6° |
| 30 Minutes | −25.9 | 150 Minutes | − 9.8 |
| 60 Minutes | −24.4 | 200 Minutes | − 9.0 (constant) |

The sugar formed in the reaction was isolated by the usual processes and distilled under diminished pressure. A clear viscous sirup was thus obtained which decolorized alkaline potassium permanganate solution in the cold and proved to be tetramethyl-γ-glucose (found: $OCH_3$, 51.3%; $n_D^{15}$ 1.4590; $[\alpha]_D$ in benzene −15.4°; b. p. 130° (0.15 mm.); quoted for tetramethyl-γ-glucose: $OCH_3$, 52.5%; $n_D^{15}$ 1.4585; $[\alpha]_D$ in benzene −17.0°; b. p. 122° (0.05 mm.)). It follows from the above sequence of reactions that the parent trimethyl methylglucoside definitely belongs to the γ-type.

**Hydrolysis of Trimethyl-γ-methylglucoside.**—This reaction was carried out under varying conditions in order to ascertain if, under any circumstances, the glucoside yields the corresponding γ-sugar.

I. A 5% solution of the glucoside in *N*/10 aqueous hydrochloric acid was kept at 100°. The rotation altered regularly from levo to dextro, and the end value $[\alpha]_D$ +65.4° was reached.

II. In this case the acid concentration was diminished to *N*/100 but otherwise the conditions were the same as in No. I. The hydrolysis was naturally slower and after twelve hours' treatment the solution had acquired the optical value $[\alpha]_D$ +40.1°, when the reaction was arrested.

III. Duplicate with Experiment II, but conducted at 60°. Here again the rotation, after the usual initial rise and fall in the levo sense, altered regularly to dextro.

In each of the above experiments the sugar was isolated by the customary processes and the product, which crystallized with unusual ease, proved to be the stable form of 2,3,6-trimethylglucose. Finally, the hydrolysis of the glucoside was conducted under the mildest possible conditions (solvent *N*/100 hydrochloric acid; *T*, 40°) and the reaction was arrested before completion. This procedure enabled the initial optical changes to be observed and revealed the presence of the α- and β-forms of the γ-type.

| | Initial | | Maximum levo | | Maximum dextro |
|---|---|---|---|---|---|
| $[\alpha]_D$ | −24.8° | ⟶ | −45° | ⟶ | +65° |

A sample of the liquid was withdrawn when the specific rotation was −5°, the acid was neutralized and the sugar isolated together with unaltered glucoside. The latter was extracted from aqueous solution by means of chloroform and showed $[\alpha]_D$ −27°, while from the aqueous portion trimethylglucose was obtained. This crystallized at once on evaporation of the solvent, and proved to be the normal variety melting at 121° and showing $[\alpha]_D$ +70° in water.

**Hydrolysis of 2,3,6-Trimethyl α- and β-Methylglucoside.**—This compound in α- and β-forms was prepared from the sugar and hydrolyzed according to the methods used by Irvine and Macdonald.[7] The results obtained were exactly as described and the dextrorotatory sugar was regenerated on heating with acids, it being observed that when obtained in this way the compound crystallized with great ease.

**Oxidation of 2,3,6-Trimethylglucose to 2,3,6-Trimethylglucono-γ-lactone.**—Six grams of crystalline trimethylglucose (m. p. 121°) was dissolved in 30 cc. of water and 7.4 g. of bromine was added drop by drop with constant shaking. During the reaction, which extended for eight hours, the liquid was thoroughly cooled in ice. The subsequent procedure was exactly as described by Purdie and Irvine,[8] the final product being purified by distillation. In this way a clear viscous liquid, b. p. 140° (0.15 mm.), was obtained while a thick sirup which also possessed the properties of a methylated lactone remained undistilled. As the molecular weight of this residue was 409 it evidently represented either a polymerized lactone or a lactide. On the other hand, the distillate proved to be the monomolecular form of 2,3,6-trimethylglucono-γ-lactone (calcd. for $C_9H_{16}O_6$: $OCH_3$, 42.2. Found: 42.6). The behavior of the compound toward sodium hydroxide was characteristic of a lactone and the correct amount of alkali was required. In addition, when dissolved in aqueous alcohol ($c$ = 1.054) the specific rotation showed the usual change, $[\alpha]_D$ decreasing from +81.5° ⟶ 74° in twenty hours. In a second preparation of the lactone by means of bromine the procedure was varied, the treatment of the acid solution with silver oxide being omitted so as to exclude the possibility of silver trimethylgluconate being formed. Obviously, the intervention of this reaction would invalidate the evidence of the experiment. After removal of the excess of bromine the product of the oxidation was extracted with chloroform and isolated. Once more the same trimethylglucono-γ-lactone was formed and the specific rotation in aqueous alcohol showed the characteristic change +91.5 ⟶ 70.3°.

**Proof that the Lactone Belongs to the γ-Series.**—The trimethyllactone was methylated in the customary manner with silver oxide and methyl iodide and, after two such treatments, the product was distilled. The clear mobile liquid thus obtained, b. p. 100–105° (0.15 mm.), $n_D$ 1.4460, proved to be tetramethylglucono-γ-lactone.

*Anal.* Calcd. for $C_{10}H_{18}O_6$: C, 51.28; H, 7.69; $OCH_3$, 52.99. Found: C, 51.0; H, 7.9; $OCH_3$, 52.1; $[\alpha]_D$ in absolute ethyl alcohol + 52.4° for $c$ = 1.867 and in aqueous alcohol +48.9° ⟶ 48.4° in twelve hours for $c$ = 1.40. On titration, 0.1375 g. required 56.5 cc. of $N/100$ sodium hydroxide (calcd., 58.5 cc.).

**Oxidation of 2,3,6-Trimethylglucose to 2,3,6-Trimethylglucono-δ-lactone.**—To a solution of 5 g. of the sugar in 50 cc. of water were added 8 g. of calcium bromide and excess of finely powdered calcium carbonate. Chlorine was led into the solution at intervals under thorough cooling and agitation, and the reaction was continued for eight hours. The calcium salts in solution were decomposed by the addition of the required amount of oxalic acid, the product extracted with chloroform and isolated in the usual manner, and finally methylated by the silver oxide reaction. On distillation, a specimen of tetramethylgluconolactone, b. p. 130° (0.8 mm.), $n_D$ 1.4534, was obtained.

*Anal.* Calcd. for $C_{10}H_{18}O_6$: C, 51.28; H, 7.69; $OCH_3$, 53. Found: C, 51.08; H, 7.79; $OCH_3$, 52.8.

The material was a mixture of γ- and δ-forms as shown by the value of the rotation, $[\alpha]_D$ +86.0° in alcohol, and by the optical change on dissolving in aqueous alcohol, when the initial specific rotation of +81.6° diminished in the course of two days to the constant value +49.6°.

[7] Irvine and Macdonald, *J. Chem. Soc.*, **127**, 1517 (1926).

[8] Purdie and Irvine, *ibid.*, **83**, 1033 (1903).

The authors desire to express their indebtedness to the Carnegie Trust for a Research Scholarship and a Research Fellowship awarded to one of them.

## Summary

1. 2,3,6-Trimethyl-γ-methylglucoside has been prepared and its constitution determined by conversion into 2,3,5,6-tetramethyl-γ-glucose. The glucoside therefore conforms to the γ-type.

2. When hydrolyzed, the liberated 2,3,6-trimethyl-γ-glucose transforms into the stable crystalline variety which is the only form isolated.

3. The oxidation of 2,3,6-trimethylglucose by bromine may lead to either the corresponding γ- or δ-lactones according to variations in the concentration of hydrogen bromide present.

4. The presence of halogen hydride is a determining factor in converting 2,3,6-trimethylglucose into the γ-form.

5. The combined results show that the formation of 2,3,6–trimethylglucose in the constitutional studies of carbohydrates by the methylation method is ambiguous as are also the results of oxidation methods in certain cases.

ST. ANDREWS, SCOTLAND

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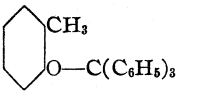
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# THE REARRANGEMENT OF TRIPHENYLMETHYL ORTHO-TOLYL ETHER

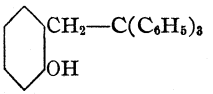
BY GEORGE S. PARSONS AND C. W. PORTER

RECEIVED SEPTEMBER 17, 1931 PUBLISHED JANUARY 7, 1932

In 1926 Schorigin[1] prepared the triphenylmethyl ether of *o*-cresol and a year later Van Alphen[2] made the corresponding derivative of phenol. These ethers rearrange when heated with hydrochloric acid or with zinc chloride. In the case of phenyl triphenylmethyl ether the triphenylmethyl group migrates from the oxygen atom to the *p*-position in the ring, as would be expected, but the change in the case of *o*-tolyl triphenylmethyl ether was reported by Schorigin and by Van Alphen as a migration of the triphenylmethyl group from the oxygen atom to the ortho side chain.




*o*-Tolyl triphenylmethyl ether




α-2-Hydroxyphenyl-β,β,β-triphenylethane

The evidence in support of this mechanism comprised the isolation of triphenylcarbinol as an oxidation product and triphenylmethane as a

[1] Schorigin, *Ber.*, **59**, 2506 (1926).

[2] Van Alphen, *Rec. trav. chim.*, **46**, 287 (1927).

reduction product of the rearranged compound. This proof of the structure was considered inadequate and we undertook to obtain more definite information concerning the nature of the final product.

We tried to oxidize the rearranged product to salicylic acid, but we were unable to obtain salicylic acid in an amount sufficient to produce a color with ferric ions. Oxidation was accomplished by dichromate and by permanganate ions but no positive test for the presence of salicylic acid could be obtained. Apparently the ring to which the hydroxyl group is attached is ruptured by the oxidizing agent. By methylating the hydroxyl group before treatment with permanganate this difficulty was overcome and methoxybenzoic acid was produced. This result confirms the claim of Schorigin and of Van Alphen.

Further evidence in support of this structure was obtained by a direct synthesis of the methyl derivative of the rearranged product through the Grignard reaction. Triphenylmethylmagnesium bromide was made by Gomberg's method[3] and an excess of this reagent was added to *o*-methoxybenzaldehyde. The addition product which formed immediately was reduced by the excess of the reagent so that, upon hydrolysis, $\alpha$-methoxyphenyl-$\beta,\beta,\beta$-triphenylethane was obtained instead of the expected secondary alcohol. This compound melts at 172°. The compound obtained from *o*-tolyl triphenylmethyl ether by rearrangement and subsequent methylation has the same melting point and the melting point is not changed when the two products are mixed.

## Experimental Part

**1. Preparation of *o*-Tolyl Triphenylmethyl Ether.**—The ether was made by warming on a water-bath a mixture of 50 g. of triphenylchloromethane and 25 g. of *o*-cresol in 200 cc. of dry pyridine for six hours. After cooling and diluting with water the product was extracted with a large volume of ether. The ether extract was freed from pyridine by washing with 6 *N* hydrochloric acid and cresol was removed by washing with 3 *N* sodium hydroxide. The ether extract was then evaporated to dryness. The residue was taken up in petroleum ether and this solution was washed with Claisen's solution (see paragraph 2) to remove the small amount of Van Alphen's "crypto phenol" which forms during the reaction and which is not removed by the treatment with aqueous sodium hydroxide. The petroleum ether extract was finally washed with water and dried and the major part of the solvent was evaporated. The precipitated product was purified by recrystallization from alcohol or from petroleum ether (m. p. 112.5°).

**2. Rearrangement of the Ether.**—Tolyl triphenylmethyl ether was converted into $\alpha$-2-hydroxyphenyl-$\beta,\beta,\beta$-triphenylethane by heating the compound with half its weight of dry zinc chloride for one hour at 180°. The product was isolated by the method described by Van Alphen[2] (m. p. 182°). The same product may be obtained in better yield from triphenylchloromethane and *o*-cresol directly by modifying the procedure described in paragraph 1. The necessary changes are (a) a higher temperature—the solution is boiled under a reflux condenser for six or eight hours, (b) a higher concentration of the reagents—only half as much pyridine being used. The product is

[3] Gomberg, THIS JOURNAL, **52**, 2455 (1930).

isolated by diluting the reaction mixture with water and extracting with ether. The ether extract is washed successively with water, dilute hydrochloric acid and dilute sodium hydroxide. It is then evaporated and the residue is taken up in Claisen's solution (50 cc. of methyl alcohol mixed with 50 cc. of 50% aqueous potassium hydroxide). The solution is filtered, then acidified, and the precipitated product is recrystallized from a mixture of ethyl alcohol and water.

3. **Preparation of the Methyl Derivative of the Rearranged Product.**—The phenol (10 g.), obtained as described in paragraph 2, was mixed with methyl iodide (50 g.) and silver oxide (25 g.) in a 300-cc. flask. Visible action began spontaneously and continued for about an hour. The mixture was then heated on a water-bath for three hours. The product was extracted with ether and recrystallized from hot alcohol (m. p. 172°).

4. **Oxidation of the Methyl Derivative.**—The methyl derivative (3 g.) in 50 cc. of glacial acetic acid was added to a solution of 3 g. of potassium permanganate in 25 cc. of water. The mixture was warmed on a water-bath for one hour, then filtered, and the filtrate was extracted with ether. The ether was washed with water until free from acetic acid and then shaken with a dilute solution of sodium hydroxide. The aqueous extract was acidified with hydrochloric acid and methoxybenzoic acid precipitated (m. p. 98°).

5. **Synthesis of α-2-Hydroxyphenyl-β,β,β-triphenylethane.**—*o*-Methoxylbenzaldehyde was made from salicylaldehyde by treatment with methyl iodide and silver oxide. The product (b. p. 242°) was dissolved in ether and treated with triphenylmethylmagnesium bromide. The addition product was hydrolyzed with warm dilute hydrochloric acid and the hydrolysis product was purified by crystallizing it from hot alcohol. This compound melted at 172° and when mixed with the methyl derivative of the rearranged product referred to in paragraph 3, the melting point was unchanged. The Grignard reagent apparently reduced the normal addition product.

*Anal.* Calcd. for α-2-methoxyphenyl-β,β,β-triphenylethane: C, 88.97; H, 6.64. Found: Product obtained by rearrangement and methylation: C, 88.4; H, 6.31. Product obtained through Grignard reaction: C, 88.8; H, 6.29.

## Summary

*o*-Tolyl triphenylmethyl ether, when heated with zinc chloride, rearranges to α-2-hydroxphenyl-β,β,β-triphenylethane. The structure of the final product has been established by direct synthesis and by the identification of oxidation products of its methyl ether.

The structure of the rearranged product corresponds to that postulated by Van Alphen and by Schorigin.

BERKELEY, CALIFORNIA

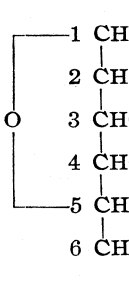
[CONTRIBUTION FROM THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

# A METHOD FOR THE IDENTIFICATION AND ESTIMATION OF THE 6-HYDROXYL GROUP IN GLUCOSE

BY JOHN WALTER HYDE OLDHAM AND JEAN KERR RUTHERFORD

RECEIVED SEPTEMBER 28, 1931 PUBLISHED JANUARY 7, 1932

It has long been known that one of the terminal hydroxyl groups of the glucose chain is sharply distinguished from the others, in that it is responsible for reducing action and for the formation of glucosides, oximes, etc. With regard to other groups the only one that may be said to be in any sense easily identified is that indexed as No. 4 in the accompanying formula, since substitution in this position prevents the formation of γ-glucosides and so, in the glucose series at least, inhibits condensation with acid methyl alcohol in the cold. The basis for this statement is the fact that of the four trimethylglucoses of the normal type only 2,3,6-trimethylglucose can exhibit this reaction. These statements definitely do not apply to the pentose series or possibly to fructose or to mannose.




Of the remaining hydroxyl groups in glucose No. 6 displays a number of special reactions, of which, however, none so far described serves as a reliable method for its identification and estimation. The first of these special reactions was described by Fischer,[1] who prepared a 1,6-dibromotriacetylglucose by acting on penta-acetylglucose with liquid hydrogen bromide. Soon afterward Purdie and Irvine[2] prepared a 2,3,4-trimethylmethylglucoside by methylating methylglucoside in presence of excess of methyl alcohol. Subsequently it was shown by one of us[3] that when position 6 is substituted by the nitrate group or by bromine these substituents can be replaced by iodine by means of sodium iodide in acetone at 100°. A more definitely useful observation was subsequently made by Helferich and collaborators,[4] *viz.*: that the triphenylmethyl group enters position 6 preferentially when triphenylmethyl chloride acts on glucose and on α- and β-methylglucoside. Work carried out more recently in this Laboratory appears to show, however, that the aromatic residue is capable of entering positions other than 6, and that in one or more of these (positions unknown) the subsequent removal of the triphenylmethyl residue is a matter of great difficulty. Finally Freudenberg[5] showed that the toluenesulfonyl group is replaceable by iodine in the 6-position of galactose, but he does not seem to have extended the

[1] Fischer, *Ber.*, **35**, 836 (1902).

[2] Purdie and Irvine, *J. Chem. Soc.*, **83**, 1028, 1037 (1903).

[3] Oldham, *ibid.*, **127**, 2840 (1925).

[4] Helferich, *Ann.*, **440**, 1 (1924); *Ber.*, **58**, 872 (1925).

[5] Freudenberg, *ibid.*, **60**, 1633 (1927).

observation beyond this point. It is obvious that none of these methods except the last could be used as a means of identifying quantitatively position 6 when unsubstituted.

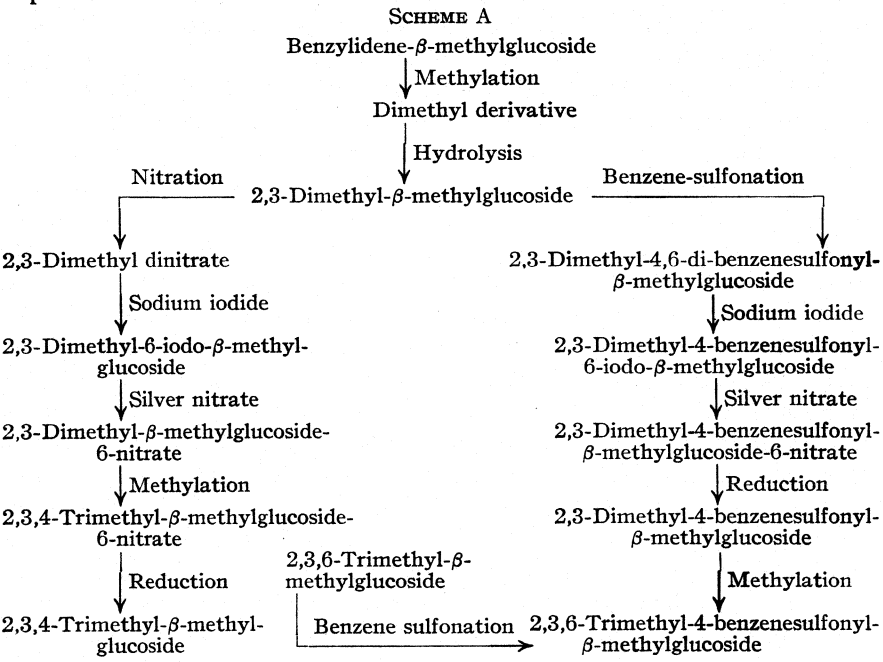
During the course of a research on starch carried out in this Laboratory by Irvine and Rutherford it became necessary to identify the components of a mixture of dimethylglucoses, and it was at first thought that the capacity of the nitrate group to be replaced by iodine was peculiar to position 6. In order to explore further the general reactions involved, experiments were begun on the crystalline dinitrate of 2,3-dimethyl-β-methylglucoside prepared as described in the experimental part. The reaction, however, followed an unexpected course, yielding besides the desired 6-iodo-2,3-dimethyl-β-methylglucoside-4-nitrate, an equal or in most cases a considerably larger quantity of 6-iodo-2,3-dimethyl-β-methylglucoside. The result is completely anomalous and it is noteworthy that no di-iodo compound was produced. In view of the behavior of the nitrate just described the corresponding benzenesulfonyl derivative was examined. The di-benzenesulfonate of 2,3-dimethyl-β-methylglucoside was found to be a crystalline substance in which one benzenesulfonyl group was replaced quantitatively by iodine in the course of heating for two hours with sodium iodide in acetone solution at 100°. It is important to limit the time of heating to two hours since prolonged treatment seems to lead also to the replacement of the 4-group and to other complications still under investigation. The first part of the research having shown that in the case of 2,3-dimethyl-β-methylglucoside di-benzenesulfonate, only the acyl group in position 6 is replaced by iodine under the conditions described, it was further extended to include the investigation of similar products obtained from the corresponding 2,3-diacetyl-β-methylglucoside, and also in a general manner to investigate as far as possible whether any other group than No. 6 shared this property and whether these observations applied only to the normal series or were equally valid for the γ-series and for anhydro compounds. In this extension of the work the *p*-toluenesulfonyl derivatives were employed as a matter of experimental convenience in place of the benzenesulfonates.

The real value of this method lies in the further fact that the iodine can be replaced by the nitrate group on boiling in acetonitrile solution with silver nitrate. The process is sufficiently accurate to be used for the estimation of iodine and has a great advantage over other methods in that it involves no loss of material. The nitrate group may in turn be converted into the hydroxyl group by the method already described[3] and thus ultimately any desired group may be introduced into position 6.

The work described in the present paper thus falls under three heads: (A) the products obtained from 2,3-dimethyl-β-methylglucoside; (B) the products obtained from the corresponding 2,3-diacetyl-β-methyl-

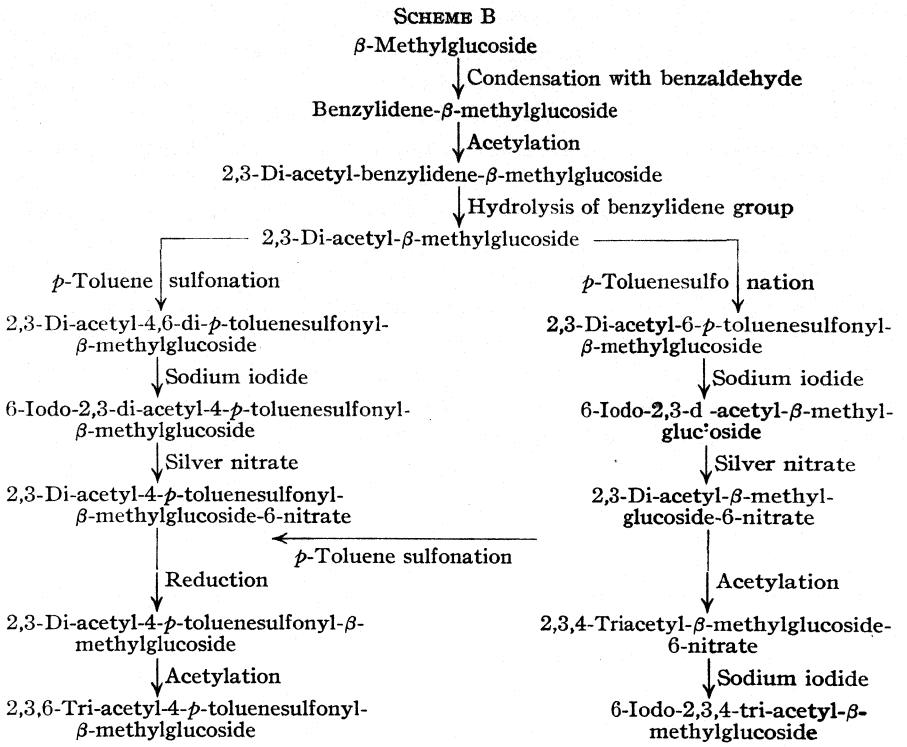
glucoside; (C) the general investigation which included the examination of a series of compounds prepared in order to study the special reactions of group No. 6.

The sections indexed A and B can best be represented schematically, notes being added where necessary, and inspection of the schemes will show that the synthetical possibilities of the sugar group have been greatly expanded.




It will be seen from the table that 2,3-dimethylglucose has been converted into 2,3,4- and 2,3,6-trimethylglucoses, respectively, and since 2,3-dimethylglucose has already been synthesized by Freudenberg[5] from 3-monomethylglucose, and by the present authors from 2-monomethylglucose, the constitution of all this series of compounds would seem to be well established.

The 2,3-di-acetyl-β-methylglucoside-4,6-dinitrate was obtained in the same way as the corresponding dimethyl compound and is equally crystalline, but on treatment with sodium iodide the reaction is not so simple as in the methylated series owing to the migration of acetyl group or to the iodine being distributed between positions 4 and 6. This is unfortunate since otherwise the dinitrate would be the best source of 2,3-di-acetyl-β-methylglucoside-6-mononitrate, which isby far the most useful and interesting of all the compounds here described. The method by which this substance is actually obtained is described in detail in the experimental part




and it is our intention to use this compound as the starting material for a number of syntheses including that of 4-monomethylglucose and β-methylcellobioside [since synthesised by Helferich, *Ber.*, **64**, 2411 (1931)].

Unfortunately, owing to the fact that these compounds cannot be deacetylated without at the same time removing the *p*-toluenesulfonyl group also, no direct link (except their common starting point) has been established between them and the methylated compounds just described. The consideration, however, of the following facts would seem to prove fairly conclusively that their constitution is similar.

(*a*) The di-acetyl-β-methylglucoside mononitrate just described undoubtedly has its nitrate group in the 6-position since it can be acetylated quantitatively to the already known tri-acetyl-β-methylglucoside-6-mononitrate.[3]

(*b*) It is also converted nearly quantitatively into the *p*-toluenesulfonyl derivative which is identical with that obtained from 2,3-diacetyl-di-*p*-toluenesulfonyl-β-methylglucoside by the series of reactions outlined above.

(*c*) It is true that these facts leave the position of the *p*-toluenesulfonyl group open to some slight doubt, but on removal of the nitrate group, followed by acetylation, a tri-acetyl-mono-*p*-toluenesulfonyl-β-methyl-

glucoside is obtained having the same melting point as that described by Helferich,[6] to which he has assigned position 4 for the *p*-toluenesulfonyl group. The allocation of this group can lie only between positions 4 and 2 since tri-acetyl-3-*p*-toluenesulfonyl and tri-acetyl-6-*p*-toluenesulfonyl-β-methylglucosides are both known and have different melting points. Tri-acetyl-2-*p*-toluenesulfonyl-β-methylglucoside is not known but it is exceedingly unlikely that the present compound should have that constitution.

The third and more general section of the research involves too many reactions to be represented schematically. In the first place the tetra-*p*-toluenesulfonyl derivative of β-methylglucoside was prepared as a crystalline compound in good yield and was converted almost quantitatively to a mono-iodo derivative, thus showing that only one group reacts under these conditions. Both these compounds owing to their extreme insolubility did not react fully with hydriodic acid, so that their methoxyl content could not be determined in the usual way. In consequence the iodo compound was converted in almost quantitative yield into the nitrate upon which an accurate methoxyl determination was carried out. In view of this and the fact that the iodine content of the iodo compound was almost the theoretical there can be little doubt concerning the composition of these substances.

In order to obtain further evidence that only position No. 6 is involved in this reaction 4,6-dimethyl-2,3-di-*p*-toluenesulfonyl α-methylglucoside (which has been recently prepared in this Laboratory by Mr. D. S. Mathers) was subjected to the sodium iodide reaction but was recovered quantitatively unchanged. In the same manner it was found that no iodine could be introduced under these conditions into the following compounds: tri-benzenesulfonyl-glucosan, 3-*p*-toluenesulfonyl-diacetoneglucose and the 2,3,6-trimethyl-5-*p*-toluenesulfonyl-β-methylglucoside obtained from 2,3,6-trimethylglucose as described below. All these facts taken together indicate that this reaction is strictly confined to the 6-position of glucose. The drawback to this method from the synthetical point of view is that no reliable process has yet been found for the subsequent removal of the *p*-toluenesulfonyl groups, but this is still under investigation and it is hoped that a means may yet be discovered.

## Experimental

**Section A.**—It may be explained that β-glucosides were employed throughout since the initial difficulty of obtaining them is more than compensated for by their great crystallizing power.

**2,3-Dimethyl-β-methylglucoside.**—This compound was obtained from the corresponding benzylidene derivative by the method described by Freudenberg.[7] The

[6] Helferich, *Ann.*, **458**, 111 (1927).

[7] Freudenberg, *Ber.*, **61**, 1750 (1928).

benzylidene residue was removed by the action of $N/20$ hydrochloric acid in acetone containing, in all, 10% of water by volume. The reaction was followed polarimetrically, the changes observed being as follows.

| Time | $\alpha$ | $[\alpha]_D$ |
|---|---|---|
| Initial | −3.28 | −65.4 |
| 30 Minutes | −2.42 | −50.7 |
| 70 Minutes | −1.51 | −42.4 |
| 100 Minutes | −1.42 | −39.5 |
| 150 Minutes | −1.43 | −39.8 |

The last four values are calculated for change in concentration due to loss of benzylidene. When hydrolysis was complete the solution was neutralized with barium carbonate, filtered, and taken to dryness in the presence of a small quantity of barium carbonate to neutralize any benzoic acid formed. The residue was dried thoroughly at 100° in a vacuum, taken up in acetone, filtered, taken to dryness and distilled at 150° (0.3 mm.). The distillate was a colorless sirup having $n_D$ 1.4690 and $OCH_3$, 40.6%; calcd. for $C_9H_{18}O_6OCH_3$, 41.8%. The yield was about 70–80%, there being always a fair residue on distillation.

| Solvent | $c$ | $[\alpha]_D$ |
|---|---|---|
| Chloroform | 4.100 | −46.9 |
| Acetone | 3.296 | −38.9 |
| Water | 3.198 | −34.3 |
| Methyl alcohol | 3.405 | −38.4 |

**2,3-Dimethyl-β-methylglucoside-4,6-dinitrate.**—In making this substance the best yield seems to be obtained on a small scale. Two typical preparations are given. In the first, 4.3 g. of substance was dissolved in 25 cc. of chloroform and the solution cooled in ice. To this was added a mixture of 45 cc. of chloroform and 30 cc. of fuming nitric acid also cooled in ice. The mixture was allowed to stand for two minutes in ice, poured into ice and water in a separating funnel, well shaken and the lower layer removed, washed with ammonium carbonate solution, dried and taken to dryness at 45°. The yield at this stage was quantitative. The product was then boiled with methyl alcohol and barium carbonate and subsequently methylated by silver oxide in the usual manner. This on isolation and treatment with ethyl alcohol gave 4.2 g. of crystals (m. p. 96–99°). The mother liquors were treated with aqueous alcoholic soda solution in ice for half an hour, the solution being thereafter flooded with water and extracted with chloroform. In this way 1.3 g. of sirup was recovered which on treatment successively with absolute alcohol and a mixture of this solvent with petroleum ether gave a further 0.5 g. of crystals, a total yield of 78% of the theoretical amount. The residue which was still largely crystalline had $OCH_3$, 32.2%; calcd. for dimethyl-β-methylglucoside-dinitrate, $C_9H_{16}O_{10}N_2$: $OCH_3$, 29.8%, and for dimethyl-β-methylglucoside-mononitrate, $C_9H_{17}O_8N$: 34.8%. In another experiment 1.5 g. of dimethyl-β-methylglucoside was treated for one minute in ice with 30% nitric acid in chloroform. The product was worked up as before, being taken to dryness, however, at 60°. On treatment with methyl alcohol, 1.3 g. of crystals was obtained in the first crop. The mother liquors were boiled with barium carbonate, giving on isolation 0.5 g. of sirup which on treatment with absolute alcohol gave about 0.3 g. of crystals and a residue of 0.1 g. which was still largely crystalline. The yield on this occasion is thus about 78%. The product can also be made by the direct action of 30% nitric acid in chloroform on the benzylidene compound, but

the yields are not so good. After one more recrystallization from absolute alcohol the product was obtained pure melting at 98–99° and crystallizing in large prisms insoluble in water and petroleum ether, sparingly soluble in ether and cold alcohols, soluble in other solvents.

*Anal.* Calcd. for $C_9H_{16}O_{10}N_2$: $OCH_3$, 29.8; N, 8.97. Found: $OCH_3$, 29.0; N, 8.97. The specific rotation was taken in chloroform when it showed $[\alpha]_D$ −20.8° for $c$ = 3.112%; $n_D$ 1.4668, approximately, for the superfused substance.

**6-Iodo-2,3-dimethyl-β-methylglucoside.**—The dinitrate obtained as above was treated with twice its weight of sodium iodide in acetone at 100° for fourteen to twenty hours. The solution colors deeply with iodine and the tube has to be opened with care as pressure develops. After taking the total solution to dryness, and treating the residue with a mixture of water and chloroform, sodium thiosulfate was added to remove iodine. Thereafter the liquid was extracted in all three times with chloroform and the extract taken to dryness. When thus obtained the product should have a refractive index greater than 1.50, otherwise it should be again put through the above reaction. The residue now consisted of a mixture of 6-iodo-2,3-dimethyl-β-methylglucoside-4-nitrate with a larger quantity of the corresponding 4-hydroxy compound. These components can be separated by extraction from benzene with water, the hydroxy compound passing into the latter, but since the former is of no interest and is usually contaminated with small quantities of the original dinitrate, it is better to convert the whole of the product into the hydroxy compound. For this purpose the total chloroform extract was taken to dryness and the residue treated with a mixture of iron dust and zinc dust in hot glacial acetic acid, this mixture of metals being more efficient than either of the two components. When no more nitrate could be detected by the diphenylamine reaction the mixture was filtered and the residue well washed with chloroform. The filtrate was poured into water and the water extracted three times with chloroform, the extract dried over potassium carbonate to remove acetic acid, and taken to dryness at 100°. The product crystallized but was too soluble in all solvents to be recrystallized. Three grams of starting material gave 2.75 g. of product, a yield of 89% of the theoretical amount. The substance crystallizes in prisms and melts at 52–55°, after previous softening at 50°. Calcd. for $C_9H_{17}O_5I$: $OCH_3$, 28.0; I, 38.2. Found: $OCH_3$, 27.4; I, 38.9. The specific rotation in chloroform was $[\alpha]_D$ −7.1° for $c$ = 3.014%; $n_D$, 1.5130, on the superfused substance.

**2,3-Dimethyl-β-methylglucoside-6-nitrate.**—This was prepared from the corresponding iodo compound by boiling the latter with an equal weight of silver nitrate in acetonitrile for two hours. Thereafter the solvent was removed in a vacuum at 100°, the well-dried residue extracted with boiling benzene, the solvent decanted, and the solid residue washed several times with benzene. In order to estimate the iodine the silver residues were dried at 100° and thereafter boiled with strong nitric acid, the silver iodide being collected and weighed. On evaporation of the benzene extract the compound was obtained as a distillable sirup soluble in all solvents except petroleum ether. 0.9827 g. of the iodo compound gave 0.760 g. of product which on distillation at 140° (0.3 mm.) gave 0.685 g. of distillate, the yields being thus 95 and 87%, respectively.

*Anal.* Calcd. for $C_9H_{17}O_8N$: $OCH_3$, 34.8; N, 5.24. Found: $OCH_3$, 33.2; N, 5.18; $n_D$ 1.4655.

The rotation in chloroform was $[\alpha]_D$ −27.7° for $c$ = 3.422%.

**Conversion of 2,3-Dimethyl-β-methylglucoside-6-nitrate into 2,3,4-Trimethyl-β-methylglucoside.**—1.2 Grams of the nitrate derivative having $n_D$ 1.4690 (obtained from 1.50 g. of the iodo compound which had not been purified by the treatment with iron dust described above) was methylated twice with silver oxide in the usual manner, giving 1.029 g. of product with $n_D$ 1.4568. This crystallized on nucleation with 2,3,4-

trimethyl-β-methylglucoside-6-mononitrate, but for purposes of identification it was converted into the parent glucoside. On reduction with iron dust in the usual manner, 0.702 g. was obtained by extraction of the aqueous solution with chloroform and a further 0.069 g. by taking the aqueous portion to dryness. Both of these products crystallized hard and on recrystallization from petroleum ether showed m. p. 93–94° which was unaffected by admixture with an authentic sample of 2,3,4-trimethyl-β-methylglucoside. The yield is thus 72% of the theoretical amount, calculating from the starting material.

**2,3-Dimethyl-4,6-di-benzenesulfonyl-β-methylglucoside.**—2.4 Grams of the dimethylmethylglucoside was treated with benzenesulfonyl chloride in pyridine for several days at the ordinary temperature. Thereafter the solid mass was treated with a mixture of benzene and water. When all was dissolved the water layer was removed and the benzene washed twice with strong hydrochloric acid and once with soda solution. It was then shaken with sodium sulfate and charcoal and taken to dryness at 100°. In this way 4.5 g. of product was obtained from the benzene and 0.226 g. of unchanged material from the first water washing. Only half of the product crystallized and this appears to be due to the fact that the benzenesulfonyl group does not easily enter position 4 when the 6-group is substituted by a large residue. As is shown below, the 6-nitrate-4-hydroxy compound reacts almost quantitatively with benzenesulfonyl chloride and is in fact the most convenient source of all these derivatives. The product consisted of slender prisms melting after two or three recrystallizations from absolute alcohol at 119–120°, insoluble in water and petroleum ether, sparingly soluble in ether and cold alcohols, soluble in other solvents.

*Anal.* Calcd. for $C_{21}H_{26}O_{10}S_2$: $OCH_3$, 18.5. Found: $OCH_3$, 18.4. The rotation in chloroform was $[\alpha]_D$ −21.0° for $c$ = 5.171%.

**6-Iodo-2,3-dimethyl-4-benzenesulfonyl-β-methylglucoside.**—The best way of preparing this substance is from the compound just described by heating in acetone for two hours at 100° with an equal weight of sodium iodide. In this way 1.5 g. of starting material gave 1.4 g. of total product. This crystallized with difficulty from methyl alcohol containing 20% of water, the crystals being washed with methyl alcohol containing 40% of water. This is not a good crystallizing medium and the yield is poor but no superior method could be found. The product, when as pure as it could be obtained, consisted of prisms melting at 72–73°, soluble in all solvents except water and petroleum ether. Calcd. for $C_{15}H_{21}O_7SI$: $OCH_3$, 19.7; I, 26.9. Found: $OCH_3$, 19.6; I, 26.9. The rotation in chloroform was $[\alpha]_D$ −7.7° for $c$ = 2.914%.

This product can also be obtained from the 6-iodo-4-hydroxy compound already described; 1.233 g. on treatment with excess of benzenesulfonyl chloride gave 1.6 g. of crude product (yield 90%). This gave 0.988 g. of crystals identical with those already described. The conversion of this substance to the corresponding nitrate is the most difficult example of this reaction yet encountered. On boiling for the usual period of two hours on one occasion the iodine content was found to be 23.2% and on another occasion only 24.2% after two consecutive treatments. As already stated the theoretical amount is 26.9%. It may be mentioned that the product from these estimations always contained iodine so that the low values quoted above cannot be due to an actual deficiency of iodine in the compound. On another occasion therefore the product was heated with silver nitrate overnight in acetonitrile at 100° when the theoretical value was obtained for the iodine content and the product contained no combined iodine. Considerable decomposition was caused, however, the yield of crude product being of the order 80%. Iodine is conveniently tested for in these compounds by heating with a little concentrated sulfuric acid, when the evolution of iodine can be easily observed.

**2,3-Dimethyl-4-benzenesulfonyl-β-methylglucoside-6-nitrate.**—This compound can

be prepared as already described but the most convenient method is by the action of benzenesulfonyl chloride in pyridine on the 6-nitrate-4-hydroxy compound already mentioned; 0.6 g. of this latter on the above treatment gave 0.053 g. of unchanged material and 0.8 g. of product from benzene. This latter gave 0.588 g. of crystals in the first crop and 0.229 g. in the second. The small residue largely crystallized on standing. The yield of crystalline material was thus of the order 90%. The product after one or two recrystallizations from absolute alcohol softened at 95° and melted at 96–97°. It consisted of prisms insoluble in water and petroleum ether, very slightly soluble in cold ethyl alcohol, rather more soluble in cold methyl alcohol and soluble in other solvents. Calcd. for $C_{15}H_{21}O_{10}SN$: $OCH_3$, 22.8; N, 3.45. Found: $OCH_3$, 22.6; N, 3.51. The rotation in chloroform was $[\alpha]_D$ −42.3° for $c$ = 5.413%.

**2,3-Dimethyl-4-benzenesulfonyl-β-methylglucoside.**—The nitrate group was reduced out as already described, 2.048 g. of starting material giving 1.793 g. of crude product or 98% of the theoretical amount. The product was crystallized from butyl alcohol and washed with low-boiling petroleum ether when it consisted of short prisms soluble in all ordinary solvents except water and petroleum ether. It melted at 86–87°. Calcd. for $C_{15}H_{22}O_8S$: $OCH_3$, 25.6. Found: $OCH_3$, 24.2. The rotation in chloroform was $[\alpha]_D$ −42.6° for $c$ = 2.498%.

**2,3,6-Trimethyl-4-benzenesulfonyl-β-methylglucoside.**—0.6 Gram of the last-mentioned compound was methylated twice with silver oxide and methyl iodide giving 0.635 g. of product. This on treatment with absolute alcohol gave 0.286 g. of material of m. p. 78–82°. The residue crystallized immediately on removal of the solvent, giving a further small crop of crystals. The yield is obviously poor but owing to its comparatively great solubility in alcohol, small amounts of impurities have a great effect in hindering the crystallization of this substance. After one further purification from absolute alcohol the product softened at 82° and melted at 83–84°. It consisted of small cubes soluble in all solvents except water and petroleum ether. Calcd. for $C_{16}H_{24}O_8S$: $OCH_3$, 32.9. Found: $OCH_3$, 31.8. The specific rotation in chloroform was $[\alpha]_D$ −35.6° for $c$ = 4.104%. Owing to the difficulty of the removal of the benzenesulfonyl residue the substance just described could not be converted into 2,3,6-trimethyl-β-methylglucoside and it became necessary to synthesize the former from the latter. For this purpose 1.0 g. of 2,3,6-trimethyl-β-methylglucoside was treated with benzenesulfonyl chloride in the usual way, when 0.7 g. of pure product was obtained which proved to be identical in melting point and mixed melting point with the compound just described.

## Section B

**2,3-Di-acetyl-benzylidene-β-methylglucoside.**—Benzylidene-β-methylglucoside was acetylated in the usual manner with acetic anhydride and sodium acetate, the mixture being poured into water and the crystals filtered off. In this way 20 g. of starting material gave 25 g. of crude product melting at 164–168°. After one or sometimes two recrystallizations from absolute alcohol the product melted sharply at 169–170°, 10.15 g. of crude crystals giving 9.7 g. of pure product. The compound crystallizes in fine needles insoluble in water and petroleum ether, sparingly soluble in cold alcohols and ether, soluble in other solvents. Calcd. for $C_{18}H_{22}O_8$: $OCH_3$, 8.47; $CH_3CO$, 23.5. Found: $OCH_3$, 8.47; $CH_3CO$, 23.9. The rotation in chloroform was $[\alpha]_D$ −95.2° for $c$ = 5.214%.

**2,3-Di-acetyl-β-methylglucoside.**—The removal of the benzylidene group was carried out as described for the corresponding dimethyl derivative the only difference being that $N/40$ acid was used on this occasion. The reaction was followed polarimetrically, the following changes being observed.

| Time | $\alpha$ | $[\alpha]_D$ |
|---|---|---|
| Initial | −4.51 | −84.4 |
| 90 minutes | −2.59 | −65.3 |
| 190 minutes | −2.19 | −55.2 |
| 250 minutes | −2.18 | −54.9 |

The last three values are calculated for change in concentration due to loss of benzylidene. The product, isolated exactly as before but not distilled, consisted of a glass insoluble in ether and petroleum ether, almost insoluble in cold benzene and soluble in other solvents. It appears to be never quite free from traces of the benzylidene compound, since on dissolving in water a small quantity of this material is deposited. The analytical figures also are low. Calcd. for $C_{11}H_{18}O_8$: $OCH_3$, 11.1; $CH_3CO$, 30.9. Found: $OCH_3$, 10.8; $CH_3CO$, 28.5. The rotation in chloroform was $[\alpha]_D$ − 55.3° for $c$ = 5.204%.

**2,3-Di-acetyl-4,6-di-*p*-toluenesulfonyl-β-methylglucoside.**—2.3 Grams of the diacetyl compound was dissolved in a little hot benzene and treated with excess of pyridine and 4.0 g. (2.5 mols) of *p*-toluenesulfonyl chloride for several days at room temperature. The product was isolated in the manner already described, 1.2 g. crystallizing out of the benzene during isolation and 3.7 g. being recovered from the benzene. The latter portion, which was sirupy, was treated with sodium iodide in the usual manner to convert it into the iodo compound and also to remove any unchanged *p*-toluenesulfonyl chloride of which there is nearly always some present; 3.3 g. was recovered from this treatment which gave 1.8 g. of crystals, a total yield of about 60% of the theoretical amount. No further quantity could be obtained by re-treating the residue with *p*-toluenesulfonyl chloride. The di-*p*-toluenesulfonyl derivative was recrystallized from absolute alcohol and consisted of needles melting at 160–161°, insoluble in water and petroleum ether, sparingly so in cold alcohols, soluble in other solvents. Calcd. for $C_{25}H_{30}O_{12}S_2$: $OCH_3$, 5.29. Found: $OCH_3$, 5.37. The rotation in chloroform was $[\alpha]_D$ −12.7° for $c$ = 5.371%.

**6-Iodo-2,3-di-acetyl-4-*p*-toluenesulfonyl-β-methylglucoside.**—2.8 Grams of the compound just described of m. p. 157–160° was treated with sodium iodide in acetone in the usual manner, giving 2.6 g. of crude product and 2.4 g. of pure substance after one recrystallization from absolute alcohol, a yield of 92% of the theoretical amount. The product, which consisted of small prisms with the same solubilities as the substance last described, melted at 160–161° (mixed with the last, 140–150°) and showed $[\alpha]_D$ in chloroform −19.9° for $c$ = 4.364%. Calcd. for $C_{18}H_{23}O_9SI$: $OCH_3$, 5.71; I, 23.3. Found: $OCH_3$, 5.65; I, 23.0. An acetyl determination carried out in the cold gave $CH_3CO$, 23.8%. Allowing for the loss of one *p*-toluenesulfonyl and two acetyl groups (calculating the latter as acetyl) the required acetyl content is 23.8%.

**2,3-Di-acetyl-4-*p*-toluenesulfonyl-β-methylglucoside-6-nitrate.**—1.001 Grams of the iodo compound was treated with silver nitrate in acetonitrile in the usual manner and worked up as already described. On crystallization from absolute alcohol, 0.756 g. was obtained in the first crop and 0.031 g. in the second, giving a total yield of crude crystals of 89% of the theoretical amount. The product was contaminated with silver and accordingly, after mixing with similar material from other preparations, it was dissolved in chloroform and filtered several times through charcoal. The solvent was removed and the residue crystallized twice from absolute alcohol. As so obtained it consisted of needles of much the same solubilities as the two last-mentioned compounds, melting at 128–129°. Calcd. for $C_{18}H_{23}O_{12}SN$: $OCH_3$, 6.49; N, 2.93; $CH_3CO$ (calculated in the same way as the last), 27.0. Found: $OCH_3$, 6.40; N, 2.81; $CH_3CO$, 27.7. The rotation in chloroform was $[\alpha]_D$ −32.9° for $c$ = 5.138%.

**2,3-Di-acetyl-4-*p*-toluenesulfonyl-β-methylglucoside.**—The nitrate was removed in

the usual manner, the product being isolated in benzene by washing with water and alkali; 1.248 g. of starting material gave a quantitative yield of crude product. This on recrystallization from absolute alcohol gave 0.943 g. in the first crop of m. p. 164–166° and 0.111 g. in the second crop of m. p. 156–161°, the total yield of crystalline material being 93%. On recrystallization from absolute alcohol it was obtained pure, melting at 165–166°, consisting of small cubes with the same solubilities as the three compounds just described. Calcd. for $C_{18}H_{24}O_{10}S$: $OCH_3$, 7.17; $CH_3CO$ (calculated as before), 29.9. Found: $OCH_3$, 7.48; $CH_3CO$, 30.5. The rotation in chloroform was $[\alpha]_D$ −55.4° for $c$ = 5.174%.

**2,3,6-Triacetyl-4-*p*-toluenesulfonyl-β-methylglucoside.**—The hydroxy compound just described was acetylated in the usual manner with acetic anhydride and sodium acetate, the mixture being poured into water and the crystalline product isolated by filtration. In this way, 1.063 g. of starting material gave 1.133 g. of crude product that melted at 110–114°, the yield being 97%. After several recrystallizations from absolute alcohol, the substance melted at 116–117° after previous softening at 115°. The melting point is indefinite but could not be improved though Helferich[6] gives the melting point of his compound which is doubtless the same as 118°. The compound crystallizes in slender prisms with much the same solubilities as the previous compounds though considerably more soluble in cold alcohols. Calcd. for $C_{20}H_{26}O_{11}S$: $OCH_3$, 6.54; $CH_3CO$ (calculated as before), 36.2. Found: $OCH_3$, 6.55; $CH_3CO$, 36.8. The rotation in chloroform was $[\alpha]_D$ −43.8° for $c$ = 5.481%.

**2,3-Di-acetyl-β-methylglucoside-6-nitrate.**—As already stated this material was first prepared from the dinitrate but the yield is too small for the method to be of much practical value. The following process was therefore adopted, which depends on the greater reactivity of the 6-hydroxyl group: 11.6 g. of diacetylmethylglucoside was treated with one molecular proportion of *p*-toluenesulfonyl chloride in pyridine for several days, giving 13.0 g. of total product and 2.6 g. of unaltered material. The product was then treated successively with sodium iodide and silver nitrate in the manner already described. The material so obtained was extracted about thirty times from benzene with water until the water washings were no longer optically active. The combined water washings were then extracted five or six times with chloroform and the latter removed in a vacuum. In this way 4.8 g. was obtained which on recrystallization from butyl alcohol gave 3.0 g. in the first crop and 0.4 g. in the second. The sirupy residue weighed 1.3 g. Calcd. for $C_{11}H_{17}O_{10}N$: $OCH_3$, 9.59. Found: $OCH_3$, 9.0. In view of its solubilities and composition the nature of this material is somewhat puzzling. The benzene residue consisted of a mixture of the 6-hydroxy- and 6-nitrate-4-*p*-toluenesulfonyl derivatives described above. The product after one further recrystallization from butyl alcohol consisted of stout prisms insoluble in petroleum ether, sparingly soluble in cold benzene and soluble in other solvents, and melted at 134–136°. Calcd. for $C_{11}H_{17}O_{10}N$: $OCH_3$, 9.59; N, 4.33; $CH_3CO$ (for two acetyl groups), 26.6. Found: $OCH_3$, 9.56; N, 4.28; $CH_3CO$, 26.7. The rotation in chloroform was $[\alpha]_D$ −29.9° for $c$ = 3.770%. On acetylation 1.7 g. of starting material gave after two recrystallizations from absolute alcohol 1.6 g. of product melting at 132–134°. The melting point of tri-acetyl-β-methylglucoside-6-mononitrate was given[3] as 133–134°. Further confirmation was obtained by converting the above 6-nitrate into the corresponding iodo compound. This when recrystallized from rectified spirit melted at 114–115°, a value identical with the melting point of 6-iodo-triacetylmethylglucoside, and showing no depression when mixed with an authentic specimen of the latter.

On treating 2,3-di-acetyl-β-methylglucoside-6-mononitrate with *p*-toluenesulfonyl chloride in the usual manner, 1.8 g. of starting material gave 2.0 g. of product (a yield

of 77%) melting when crude at 127–129° and showing no alteration when mixed with the 2,3-di-acetyl-4-*p*-toluenesulfonyl-6-nitrate described above, thus finally proving the constitution of 2,3-di-acetyl-β-methylglucoside-6-mononitrate.

## Section C

**Tetra-*p*-toluenesulfonyl-β-methylglucoside.**—Two grams of β-methylglucoside was treated with excess of *p*-toluenesulfonyl chloride in the usual manner for about a week. The hard mass was thereafter rubbed up with a mixture of alcohol and glacial acetic acid in the cold, the crystals filtered off and washed with more alcohol. In this way 8.9 g. of material was obtained. This was then boiled with enough glacial acetic acid to make a fairly fluid system, but not enough to dissolve the whole of the material. On cooling and filtering, 6.9 g. of product was obtained of m. p. 171–176°, a yield of about 82%. Only 0.3 g. of a stiff sirup was isolated from the various washings. The product after crystallization from glacial acetic acid consisted of very minute prisms melting with decomposition at 177–178°. It was fairly soluble in hot glacial acetic acid, but sparingly soluble or insoluble in all cold solvents. Owing to its insolubility in hydriodic acid the methoxyl content could not be determined. The specific rotation in chloroform was $[\alpha]_D$ −6.6° for $c$ = 3.170%.

**6-Iodo-2,3,4-tri-*p*-toluenesulfonyl-β-methylglucoside.**—One and one-half grams of the compound described above on treatment with sodium iodide in the usual manner gave 1.3 g. of crude product, a yield of about 93%. This on recrystallization from much glacial acetic acid gave 1.1 g. of pure product consisting of long fine prisms melting at 211–212° and even more insoluble than the last compound, being very sparingly soluble in hot glacial acetic acid. It may be mentioned that a large proportion of this substance crystallizes out from the acetone on cooling after the treatment with sodium iodide described above, and may be isolated by filtering and washing the residue with water and alcohol. As in the case of the compound last described it was not possible to determine methoxyl. The iodine was, however, determined in the usual way by conversion into the nitrate derivative. Calcd. for $C_{28}H_{31}O_{11}S_3I$: I, 16.57. Found: I, 16.49. The specific rotation in chloroform was −1.2° for $c$ = 3.269%.

**2,3,4-Tri-*p*-toluenesulfonyl-β-methylglucoside-6-mononitrate.**—Owing to the extreme insolubility of the iodo compound the treatment with silver nitrate had to be slightly modified; 1.564 g. of the iodo compound was boiled with 3.0 g. of silver nitrate in acetonitrile for four hours, the product being thereafter isolated in the usual manner, when 1.372 g. of total product was obtained. This was crystallized from glacial acetic acid giving 1.163 g. in the first crop and 0.077 g. in a second crop. The yield of crystalline material was thus about 86% of that theoretically possible. The product consisted of minute prisms, sintering at 154°, melting at 166–168° and having rather greater solubilities than the two preceding substances. This is shown by the fact that the compound gives an accurate value for the methoxyl content. Calcd. for $C_{28}H_{31}O_{14}S_3N$: $OCH_3$, 4.42; N, 1.99. Found: $OCH_3$, 4.43; N, 1.74. The specific rotation in chloroform was −21.1° for $c$ = 5.638%. Since this compound was made only for the sake of getting an accurate value for the methoxyl content, it has not been further examined.

**2,3,4-Tri-benzenesulfonyl-glucosan.**—For reasons stated in the introduction the action of sodium iodide in acetone on this and the following compounds was investigated. The present compound was prepared some years ago in this Laboratory by the action of benzenesulfonyl chloride on glucosan in the usual manner, the yield being good. The product crystallized from glacial acetic acid in short prisms which sintered at 146° and melted at 147–148°. Since sulfur estimations in this series are not very satisfactory the compound was submitted to the action of acetylating agents, from which

it was recovered quantitatively unchanged, a result which showed it to be fully substituted, and that the constitution assigned to it was correct. On treatment with sodium iodide in the usual manner it was recovered quantitatively unchanged.

**2,3,6 - Trimethyl - 5 - *p*-toluenesulfonyl - γ - methylglucoside.**—2,3,6 - Trimethyl - γ - methylglucoside prepared from 2,3,6-trimethylglucose was treated with one molecular proportion of *p*-toluenesulfonyl chloride and the product isolated in the customary manner. The sirup so obtained was treated with sodium iodide in acetone but no trace of iodine could be found in the resulting product. The authors wish to express their thanks to Mr. C. Miller for carrying out this portion of the work.

As already stated the action of sodium iodide in acetone was also tried on the *p*-toluenesulfonyl derivative of glucosediacetone which was prepared in the manner already described by Freudenberg[5] and on 4,6-dimethyl-2,3-di-*p*-toluenesulfonyl-α-methylglucoside which has been recently prepared in this Laboratory by Mr. D. S. Mathers, who kindly gave us a specimen, but in both cases the compounds were recovered quantitatively unchanged.

The authors desire to acknowledge their indebtedness to the Carnegie Trust for the facilities provided during the foregoing research. They also take this opportunity of expressing their gratitude to Principal Sir James Irvine, LL.D., F.R.S., for the invaluable help which he has given.

## Summary

1. Position 6 in the glucose chain can be identified (when not already substituted) by conversion of the sugar into the corresponding glucoside, substituting the vacant hydroxyl groups by *p*-toluenesulfonyl residues, and heating the product with sodium iodide in acetone at 100°.

2. Under these conditions the *p*-toluenesulfonyl substituent in position 6 is replaced by iodine quantitatively.

3. The iodo compound can be quantitatively estimated for iodine by boiling with silver nitrate in acetonitrile. This yields the corresponding nitrate, which can be subsequently converted into the corresponding hydroxy compound, thereby affording an accurate identification and estimation of the 6-hydroxy group in glucose.

4. Evidence has been collected to show that these properties are strictly confined to the 6 position of glucose.

5. A number of partially substituted glucose derivatives have been prepared for the first time by means of these reactions.

6. The ease with which the various compounds crystallize enables the reactions to be carried out on the small scale and the synthetical application of the results is being explored in this Laboratory.

ST. ANDREWS, SCOTLAND

[CONTRIBUTION FROM THE SCHOOL OF PHARMACY AND THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

# THE CONDENSATION OF ALDEHYDES AND KETONES WITH ORTHO-AMINOTHIOPHENOLS, BENZOTHIAZOLINES AND BENZOTHIAZOLES. II

BY HERMAN P. LANKELMA AND PHILIP X. SHARNOFF

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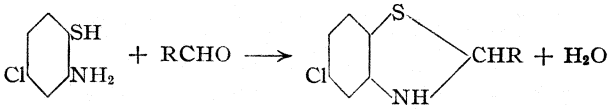
In a previous paper[1] it was shown that aldehydes condense with 2-amino-4-chlorothiophenol to give benzothiazolines.




A number of benzothiazolines were described in which the radical R was both aliphatic and aromatic. These substances were shown to be very easily oxidized to the corresponding benzothiazole, especially if R is an aromatic radical.

In the present work this reaction has been further studied to include the more common aliphatic aldehydes through valeraldehyde as well as several derivatives of benzaldehyde. With aliphatic aldehydes only benzothiazolines were obtained as the condensation products; the aromatic aldehydes employed, however, unlike the previous cases studied, gave only benzothiazoles under the same conditions.[2]

α-Unsaturated aldehydes gave only resinous products although a number of condensing agents were used. In one case, cinnamic aldehyde, the benzothiazole was separated in small yield.

The derivatives of aliphatic and aromatic aldehydes are easily obtained as pure crystalline solids. Since the reagent 2-amino-4-chlorothiophenol is easily prepared, these derivatives may be conveniently used for the identification of aldehydes.

Previous attempts to condense *o*-aminothiophenol with ketones have been unsuccessful.[3]

By using the method employed with aldehydes and prolonging the reaction time, we were able to obtain benzothiazolines from certain ketones. The spiro compounds obtained from cyclopentanone and cyclohexanone are highly colored, amethyst and dark blue, respectively.

## Experimental

**Preparation of Benzothiazolines and Benzothiazoles.**—The method employed was the same as that used in previous work. One mole of 2-

[1] Lankelma and Sharnoff, THIS JOURNAL, **53**, 2654 (1931).

[2] Evidence has previously been presented to show that this failure to obtain benzothiazolines is due to oxidation in the process of purification.[1]

[3] Bogert and Stull, THIS JOURNAL, **47**, 3078 (1925).

TABLE I

PROPERTIES AND ANALYTICAL DATA OF ALDEHYDE AND KETONE DERIVATIVES

| Aldehyde or ketone | Product Benzothiazoline | M. p., °C. | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Chlorine, % Calcd. | Chlorine, % Found |
|---|---|---|---|---|---|---|---|---|---|
| Butyric | 2-Propyl-5-chloro-[a] | 49 | $C_{10}H_{12}NClS$ | 56.15 | 56.17 | 5.67 | 5.57 | | |
| Isobutyric | 2-Isopropyl-5-chloro-[a] | 45 | $C_{10}H_{12}NClS$ | 56.15 | 56.48 | 5.67 | 5.53 | | |
| Valeric | 2-Butyl-5-chloro-[a] | 78 | $C_{11}H_{14}NClS$ | 57.97 | 58.21 | 6.21 | 6.14 | | |
| Isovaleric | 2-Isobutyl-5-chloro-[a] | 69 | $C_{11}H_{14}NClS$ | 57.97 | 58.04 | 6.21 | 6.32 | | |
| Phenylacetic | 2-Benzyl-5-chloro-[a] | 89 | $C_{14}H_{12}NClS$ | 64.20 | 64.54 | 4.62 | 4.62 | | |
| | Benzothiazole | | | | | | | | |
| Furfural | 2-Furyl-5-chloro-[a] | 122 | $C_{11}H_6ONClS$ | 56.00 | 56.15 | 2.56 | 2.78 | | |
| *m*-Nitrobenz- | 2-(3′-Nitrophenyl)-5-chloro-[b] | 146 | $C_{13}H_7O_2N_2ClS$ | 53.65 | 53.90 | 2.43 | 2.54 | | |
| Salicylic | 2-(2′-Hydroxyphenyl)-5-chloro-[c] | 201 | $C_{13}H_8ONClS$ | 59.63 | 59.78 | 3.08 | 3.22 | 13.56 | 13.80 |
| Vanillin | 2-(3′-Methoxy-4′-hydroxyphenyl)-5-chloro-[d] | 173 | $C_{14}H_{10}O_2NClS$ | 57.59 | 57.48 | 3.45 | 3.67 | 12.16 | 12.37 |
| Piperonal | 2-(3′,4′-Methylenedioxyphenyl)-5-chloro-[d] | 173 | $C_{14}H_8O_2NClS$ | 57.99 | 57.75 | 2.78 | 2.88 | 12.24 | 12.22 |
| Cinnamic | 2-Styryl-5-chloro-[a] | 134 | $C_{15}H_{10}NClS$ | 66.25 | 66.52 | 3.71 | 3.63 | 13.05 | 13.04 |
| | Benzothiazoline | | | | | | | | |
| Acetone | 2,2-Dimethyl-5-chloro-[a] | 37 | $C_9H_{10}NClS$ | 54.08 | 53.72 | 5.05 | 5.11 | 17.80 | 18.07 |
| Acetophenone | 2-Methyl-2-phenyl-5-chloro-[a] | 71 | $C_{14}H_{12}NClS$ | 64.20 | 64.03 | 4.62 | 4.57 | 13.55 | 13.69 |
| Cyclohexanone | 5′-Chloro-spiro-(1-cyclohexane-2′)[a] | 93 | $C_{12}H_{14}NClS$ | 60.07 | 59.73 | 5.93 | 5.97 | 14.82 | 14.82 |
| Cyclopentanone | 5′-Chloro-spiro-(1-cyclopentane-2′-)[a] | 47 | $C_{11}H_{12}NClS$ | 58.48 | 58.31 | 5.32 | 5.23 | | |

[a] Solvent, alcohol. [b] Butyl alcohol. [c] Xylene. [d] Propylene glycol.

amino-4-chlorothiophenol hydrochloride was dissolved in pyridine and one mole of the aldehyde or ketone was added dropwise to the warm solution. The mixture was finally heated on the water-bath. A few minutes to a half hour of heating sufficed for the aldehydes; the ketones required from one to six hours. The condensation product was precipitated by acidifying the cold solution.


## Summary

1. Aliphatic aldehydes condense with 2-amino-4-chlorothiophenol to give benzothiazolines; aromatic aldehydes may give a benzothiazoline or a benzothiazole, depending upon the aldehyde employed.

2. Certain ketones condense with 2-amino-4-chlorothiophenol to give benzothiazolines.


CLEVELAND, OHIO

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

# NATURAL AND SYNTHETIC RUBBER. VIII. PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF SODIUM RUBBER

BY THOMAS MIDGLEY, JR., A. L. HENNE AND A. F. SHEPARD

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In the first paper[1] of this series it was shown that the pyrolysis products of natural rubber are directly related to the rubber molecule. The pyrolysis products of sodium rubber should bear a similar relationship to its molecular structure, and the difference between its formula and that of natural rubber should be detected by a study of these products.

Four kilograms of sodium rubber was destructively distilled. The resulting hydrocarbons were separated by fractional distillation, and identified by the methods previously employed.[1] The results are summarized in Table I. The starred compounds were identified by methods described in the experimental part. The components marked "abridged" were noted during the course of the fractionation, but were not investigated more fully due to the limited amount of available material.

The sodium rubber used was benzene free. Hence the presence of benzene among the distillation products confirms the viewpoint of its origin as expressed in paper I.

*m*-Xylene is not the only xylene formed. This agrees with the expectations based on the structure of sodium rubber indicated in a previous paper.[2] Mass action considerations predict the ratio of ortho:meta:para-xylene as 5:10:5, but actually it is found to be $<1:10:2$. The reduction of the *o*-isomer can be explained by the assumption made in paper I that free valences on secondary or tertiary carbon atoms will accept hydro-

[1] Midgley and Henne, THIS JOURNAL, **51**, 1215–1226 (1929).

[2] Ref. 1, pp. 1294–1296.

TABLE I

COMPOUNDS, IDENTIFICATIONS AND QUANTITIES

| Compounds | Degree of identification | Percentage in distillate |
|---|---|---|
| Propylenes and butenes | Positive | 0.3 |
| $CH_3CH(CH_3)CH{=}CH_2$ | Positive | 0.2 |
| $CH_2{=}C(CH_3)CH_2CH_3$ | Positive | 2.0 |
| $CH_2{=}C(CH_3)CH{=}CH_2$ | Positive | 1.1 |
| $CH_3C(CH_3){=}CHCH_3$ | Positive | 4.2 |
| Component boiling at 58° | Abridged | 0.05 |
| 3-Methylpentenes | Positive | .4 |
| Component boiling at 68° | Abridged | .1 |
| *Benzene | Positive | .1 |
| *Isomeric heptane | Positive | .03 |
| Component boiling at 93–95° | Abridged | .1 |
| Tetrahydrotoluene | Positive | .4 |
| Toluene | Positive | .1 |
| Component boiling at 121–122° | Abridged | .2 |
| *Hexahydroxylene | Possibly present | .1 |
| *o-Xylene | Uncertain | .006 |
| *m-Xylene | Positive | .1 |
| *p-Xylene | Positive | .02 |
| Compounds with 9 carbon atoms | Similar to those from natural rubber but not investigated | .5 |
| *Compounds with 10 carbon atoms | Similar to those from natural rubber but in too small an amount to separate properly | 6.4 |
| *Dipentene | Uncertain | 0.1 |

Normal pentane, isopentane and dihydroxylene were absent.

gen rather than form rings. This does not explain the decrease of the *p*-isomer. It may be assumed that during the polymerization of isoprene, a directive force causes the 1,4-type of linkage of isoprene units to be favored. The result is a molecule more nearly resembling the natural rubber molecule in methyl group spacing than would be expected.[3]

## Discussion

The comparison of the foregoing table with the similar table in paper I of this series is of primary interest. The significant similarities and differences in the pyrolysis products may be summarized as follows.

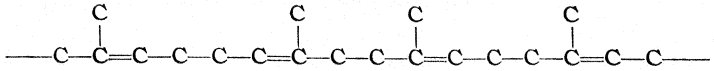
The arrangements of carbon atoms in the compounds obtained from natural and sodium rubber are the same, except for the position of some methyl groups. Compounds with five and ten carbon atoms predominate in both cases.

The products obtained from sodium rubber are more saturated. This is shown by the decrease of the quantities of isoprene and dipentene, the increase of the amount of pentenes, and the appearance of small amounts

[3] Steimmig, *Ber.*, **47**, 350 (1914), has made a similar observation in his work on the ozonation of various synthetic rubbers.

of saturated hydrocarbons. The last were entirely absent in the natural rubber distillate.

These results together with the postulates of paper I confirm the carbon arrangement in the sodium rubber formula



but disagree with the conception of a recurring double bond. Bromine titration indicates one double bond per $C_5H_8$ unit. Ozonation gives an ozonide ($C_5H_8O_3$), but this ozonide does not break down on heating with water to give the simple compounds expected.[4]

Overvulcanized rubber behaves, in many respects, like sodium rubber. It still has one double bond for each sulfur-free $C_5H_8$ unit, as shown by the fact that these will accept two atoms of bromine, or one molecule of ozone. The ozonide is not severed into simple molecules by treatment with water. Pyrolysis yields little isoprene or dipentene, but considerable amounts of pentenes and decomposition products which are substantially the same as those obtained from sodium rubber.

Hence it may be concluded that the structural formula of sodium rubber is a modification of the one given above involving hydrogen migration or cyclization of such a nature that one chemically weak bond results for each $C_5H_8$ group and that this formula is a sulfur-free example of a rearrangement that occurs to some extent during the vulcanization of natural rubber.

## Experimental Part

The sodium rubber used in this work was prepared by polymerizing boiling isoprene with liquid sodium–potassium alloy. The isoprene was prepared by the careful fractionation of the pyrolysis products of crepe rubber; it boiled at 31–35°, contained no benzene, and titration indicated 1.8 double bonds. The unpolymerized material was removed from the rubber by distilling from a steam-bath. The distillate consisted chiefly of 2-methyl-1-butene and 2-methyl-2-butene together with about 25% of unpolymerized isoprene.

A 3.86-kg. batch of this rubber which still contained the sodium–potassium alloy[5] was then destructively distilled in the manner previously described.[1] A con-

[4] Harries, *Ann.*, **383**, 217 (1911); **395**, 241 (1913); **406**, 180 (1914).

[5] The presence of sodium–potassium alloy is not primarily responsible for the relatively low unsaturation of sodium rubber distillates. This is shown by the percentages of isoprene yielded in the fractions boiling from 32–38° on pyrolysis of 100 g. batches of the following

| | |
|---|---|
| Crepe rubber | 65% isoprene |
| Crepe rubber + 6% Na–K | 55% isoprene |
| Sodium rubber, alloy free | 35% isoprene |
| Sodium rubber + 1% Na–K | 18% isoprene |

denser cooled with carbon dioxide snow was used to catch the more volatile materials. This condensate was warmed to room temperature and the escaping vapor passed into a solution of bromine in carbon tetrachloride. Fractional distillation yielded only 35 g. of propylene and butene dibromides boiling at 140–162° and having $d_4^{20}$ 1.78.

The remainder of the hydrocarbons were separated and identified by the same methods as were previously employed, except as specifically mentioned hereafter. Due to the limited amount of material available, the complete identifications of certain minor constituents were omitted to make possible the investigation of other more important points. These cases are marked "abridged" in Table I.

**Benzene.**—The method of Rhodes, Gardner and Lewis[6] was first employed to investigate the presence of benzene in a cut boiling at 76–80°. In ethylene bromide this cut showed a mean molecular weight of 87. In benzene, molecular weights of 107.5, 110 and 107 were found. The presence of 17.5% of benzene is thus indicated. The remainder of the cut was then brominated and steam distilled. After treatment with sulfuric acid, nitration gave dinitrobenzene, which was purified and identified by a mixed melting point determination with authentic material.

The formol reaction of Linke[7] was used to establish the absence of any significant quantity of benzene in the isoprene from which the rubber was prepared. This reaction detects less than 0.1% of benzene in petroleum ether. A mixture of 25 cc. of isoprene and 2 cc. of pure *n*-heptane was saturated with bromine at 0° and the product steam distilled to bring over the heptane. The heptane was washed three times with concentrated sulfuric acid, and three drops of it were added to a mixture of 3 cc. of concentrated sulfuric acid and 2 drops of formaldehyde. No precipitate was formed. When the test was repeated with 0.02% benzene added to the isoprene, the characteristic precipitate was obtained in abundance.

**Xylenes.**—By bromination and steam distillation of several cuts boiling from 134–142°, a fraction rich in xylene was isolated. This fraction boiled at 136–142° and had $d_4^{20}$ 0.827, $n_D^{20}$ 1.4630 and a molecular weight in benzene of 112 and 112. The presence of a saturated hydrocarbon along with xylenes is thus indicated. A portion of this material was nitrated by the procedure of Mulliken[8] and the crude mixture of nitro compounds was subjected to crystallization from alcohol; 77% of the nitro compound was recovered as trinitro-*m*-xylene, which was identified by a mixed melting point with authentic material.

*Anal.* Calcd. for $C_8H_7N_3O_6$: N, 17.42. Found: N, 17.29, 17.36.

From the mother liquors were obtained by recrystallization 14% of trinitro-*p*-xylene identified by a mixed melting point with authentic material.

An attempt was made to determine quantitatively the amounts of *o*- and *p*-xylenes present by a method similar to that used for benzene. The method was not quantitatively satisfactory due to the abnormal behavior of *o*- and *p*-xylenes as cryoscopic solvents. The results, however, did agree qualitatively with those obtained by the nitration method.

The oxidation of a small amount of the crude xylenes with potassium permanganate produced an acid which gave the fluorescein test for phthalic acid. This is evidence of the presence of *o*-xylene in small amount, estimated to be less than 0.006% of the original rubber.

**Compounds with Ten Carbon Atoms.**—More than 6% of the total distillate con-

[6] Rhodes, Gardner and Lewis, *Ind. Eng. Chem.*, **20**, 85 (1928).

[7] Linke, *Ber. deut. pharm. Ges.*, **11**, 258–262 (1901); *Chem. Centr.*, II, 130 (1920).

[8] S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, **1904**, Vol. I, p. 202.

sisted of compounds boiling from 158–176°. Prolonged fractionation failed to separate the components satisfactorily; fractionation from aniline was likewise of little value. Molecular weight determinations in benzene for the fractions in this range gave values from 133–139°. The two largest cuts in this range were examined more closely after aniline fractionation. The cuts boiled at 160–162.5° and 173–5.5° on Engler distillation and each comprised about 30% of the material boiling from 158–176°. The experimental data concerning these components are summarized below.

**Component 160–162.5°:** $d_4^{20}$ 0.826; $n_D^{20}$ 1.4627; mol. wt. in benzene 133, 133; double bonds 1.15. Combustion showed C, 87.44, 87.58; H, 12.14, 12.19, which is an empirical composition of $C_{10}H_{16.5}$. On hydrogenation 1.2 moles of hydrogen were absorbed. The resulting material boiled at 162–164°, and had $d_4^{20}$ 0.791, $n_D^{20}$ 1.4369, and mol. wt. in benzene 138, 139.

**Component 173–175.5°:** $d_4^{20}$ 0.837; $n_D^{20}$ 1.4709; mol. wt. in benzene 137, 136; double bonds 1.6. Combustion gave C, 87.61, 87.79; H, 12.15, 12.03, which is an empirical formula of $C_{10}H_{16.4}$. On hydrogenation 1.7 moles of hydrogen were absorbed; the product boiled at 170.5–172.5° and had $d_4^{20}$ 0.804, $n_D^{20}$ 1.4425 and mol. wt. in benzene of 139, 139. No dipentene tetrabromide could be obtained when the original hydrocarbon was brominated.

**Saturated Compounds.**—Various cuts were examined for saturated compounds by brominating, steam distilling, washing with sulfuric acid, redistilling and finally nitrating with mixed acid, washing with sulfuric acid and again redistilling. The observations are tabulated.

| Boiling range, °C. | $d_4^{20}$ | $n_D^{20}$ | Mol. wt. | Percentage in total distillate | Remarks |
|---|---|---|---|---|---|
| *ca.* 75 | | | | 0.003 | Presence evident from low density and refractive index of benzene specimen. |
| 92–93 | 0.726 | 1.4023 | | .03 | Paraffin hydrocarbon present. |
| 119–122 | .765 | 1.4203 | 112, 112.5 | .1 | Naphthenic hydrocarbon present, presumably hexahydroxylene |
| 136–142 | .78[a] | | 118[a] | .1 | Presumably a naphthenic hydrocarbon. |

[a] The properties of this material were extrapolated from those of the xylene fraction after determination of the amount of saturated hydrocarbon by the procedure of Spielman and Jones.[9]

**Ozonation of Sodium Rubber and of Overcured Rubber.**—The sodium rubber was purified before ozonation by the following procedure. A sample was dissolved in benzene, and alcohol was slowly added to react with the sodium–potassium alloy and to precipitate the rubber. The rubber was boiled out with water and then redissolved in benzene and reprecipitated with alcohol twice more. After removal of solvents in vacuum, a double bond determination by the method of Lewis and McAdams[10] showed the presence of 1.0 double bond per $C_5H_8$ unit.

The overcured rubber was prepared by curing a rubber–sulfur mix for 150 hours at 150°. Analysis showed 5.7% combined sulfur and 0.11% free sulfur; a double bond determination indicated 0.84 double bond per $C_5H_8$ unit.

[9] Spielman and Jones, *J. Soc. Chem. Ind.*, **36**, 489–490 (1917)

[10] Lewis and McAdams, *Ind. Eng. Chem.*, **12**, 673 (1920).

Ozonation of the samples was carried out in carbon tetrachloride to which 5% of glacial acetic acid was added. Solvent loss was made up by adding more acetic acid. The sodium rubber was soluble in this mixture, while it was necessary to grind the overcured rubber finely and suspend it in the solution. Solvents were removed from the ozonides in high vacuum. On boiling the ozonides with water only traces of material of low molecular weight were obtained. In each case about half the ozonide was dissolved by the water and could be thus separated; the remainder formed a solid Analyses of the ozonides and of various fractions separated by water are given in Table II. The sample of sodium rubber ozonide had turned very black during the removal of solvents in vacuum.

TABLE II

ANALYSES OF OZONIDES

| | C, % | | H, % | | S, % | | Empirical formula |
|---|---|---|---|---|---|---|---|
| Sodium rubber ozonide | 54.65 | 55.05 | 7.29 | 7.43 | | | $C_5H_8O_{2.6}$ |
| Water-insoluble material from sodium rubber ozonide | 65.37 | 65.47 | 7.55 | 7.45 | | | $C_5H_{6.8}O_{1.55}$ |
| Overcured rubber ozonide | 53.39 | 53.30 | 6.44 | 6.46 | 4.57 | 4.45 | $[(C_5H_8S)(C_5H_8O_3)_{6.14}]_n$ |
| First water extract from overcured rubber ozonide | 49.2 | | 6.6 | | 1.86 | 1.97 | ..... |
| Second water extract from overcured rubber ozonide | 52.64 | 52.55 | 6.23 | 6.43 | 4.66 | 4.80 | ..... |
| Solid insoluble in water from overcured rubber ozonide | 61.21 | 61.28 | 6.16 | 6.18 | 5.32 | 5.38 | ..... |

## Summary

The pyrolysis products of sodium rubber have been compared with those of natural rubber. They indicate that sodium rubber is isomeric with natural rubber in the positioning of its methyl groups, and that the double bond of sodium rubber differs from the true ethylenic bond of natural rubber. In the latter respect sodium rubber closely resembles overvulcanized rubber.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# THE PARTITION PRINCIPLE AS APPLIED TO THE STRUCTURE OF ENOLIC SODIUM DERIVATIVES OF 1,3-DIKETONES AND BETA-KETO ESTERS. II[1]

BY ARTHUR MICHAEL AND JOHN ROSS

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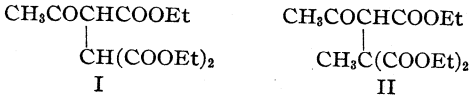
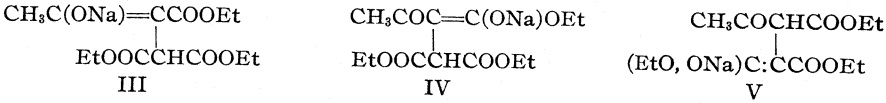
In a wide number of cases the sodium enolates of β-keto esters and 1,3-diketones react with chlorocarbonic ester to give mainly, or even entirely, the O-carbethoxy derivative. The sodium enolates of the keto esters, *e. g.*, acetoacetic,[2] acetomalonic,[3] α-alkyl acetoacetic[4] and of the diketones, *e. g.*, acetylacetone,[5] benzoylacetone[6] belong to the type RC(ONa)=C(X, Y) in which the formation of an α-carbon derivative is the only alternative to the formation of an O-carbethoxyl derivative. With the sodium enolate of α-aceto-α′-carbethoxysuccinic ester (I) it should be possible to obtain C-derivatives at the α- and α′-carbon atoms as well as the O-carbethoxyl derivative.

In a recent communication,[7] it was shown that upon treating the sodium enol derivative of (I) with methyl iodide, methylation occurred entirely upon the malonic residue, giving the compound (II).



I II

This result was interpreted as indicating the greater reaction velocity of the malonic enolate group with methyl iodide, as compared with that of the acetoacetic enolate group. From a consideration of the relative degree of neutralization of the sodium in the possible sodium enolates III, IV and V, it was concluded that the sodium in III was neutralized to such a degree as to be almost inactive toward methyl iodide in the cold.



III IV V

Toward sodium enolates, chlorocarbonic ester is a much more reactive compound than methyl iodide. With sodium enol malonic ester, chlorocarbonic ester yields methanetricarboxylic ester and the study of the

[1] Part I of this series of investigations appeared in THIS JOURNAL, **53**, 2394 (1931).

[2] Michael, *J. prakt. Chem.*, **37**, 474 (1888); **45**, 583 (1892); *Am. Chem. J.*, **14**, 491 (1892).

[3] Auwers and Auffenberg, *Ber.*, **51**, 1101 (1918).

[4] Michael, *Am. Chem. J.*, **14**, 491 (1892).

[5] Claisen, *Ann.*, **277**, 176 (1893).

[6] Michael and Ross, THIS JOURNAL, **53**, 2401 (1931).

[7] Michael and Ross, *ibid.*, **53**, 2394 (1931).

products of reaction with chlorocarbonic ester on the sodium derivative of enol-$\alpha$-acetyl $\alpha'$-carbethoxysuccinic ester (I) is therefore of interest as affording information whether the more reactive chlorocarbonic ester would form an O-carbethoxyl derivative in preference to a C-derivative at the acetoacetic or malonic residue, or a mixture of these derivatives.

$\alpha$-Acetyl-$\alpha'$-carbethoxysuccinic ester (I) was previously prepared by Gault and Klees[8] by the action of $\alpha$-chloroacetoacetic ester upon sodium enol malonic ester in toluene. A number of other products were formed, among these a liquid ester, b. p. 170–175,° which they regarded as the corresponding enol form (VI). It gave a red color with alcoholic ferric chloride, and an acetyl derivative upon treatment with acetic anhydride, but it gave no reaction with phenylhydrazine, semicarbazide acetate or hydroxylamine. It was also noted that the ester did not add bromine, but this was thought to be due to rearrangement to the keto form by the catalytic action of the bromine.[9]

$$\begin{array}{l} CH_3C(OH)=CCOOEt \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH(COOEt)_2 \end{array} \qquad \text{VI}$$

In a second paper,[10] these authors examined the action of chloromalonic ester upon sodium enol acetoacetic ester and in this reaction they obtained a much more satisfactory yield of $\alpha$-acetyl-$\alpha'$-carbethoxyl succinic ester (I) and the product crystallized, m. p. 34°. This solid was regarded as the keto form of the liquid ester first obtained, since it gave a semicarbazone, a phenylhydrazone, but no color with alcoholic ferric chloride. The solid ester disssolved in alkali, and, upon acidifying the alkali solution, a mixture of the solid and a liquid ester was obtained. The latter was regarded as the enol form (VI) since when treated with hydrogen bromide it gave the solid ester.

Previously,[6] we have described $\alpha$-aceto-$\alpha'$-carbethoxy succinic ester as a liquid, b. p. 147° (2 mm.), which gave a red color with alcoholic ferric chloride and a semicarbazone, m. p. 76°, with semicarbazide acetate. It has been possible by long cooling of the liquid ester to obtain the solid form, m. p. 34°, and, once obtained, no difficulty was experienced in crystallizing out this form from the liquid product. The ester, obtained pure by several crystallizations from ligroin, gave a purplish-red color a few seconds after mixing with alcoholic ferric chloride. Bromine titration by the Meyer indirect method indicated the presence of 0.3% enol in a methyl alcohol solution. Titration of a sample immediately after distillation from a Pyrex glass flask gave a value of 1.6% enol content. An attempt was made to liberate the enol from the sodium salt at $-10°$; a solid ester, m. p. 34° and

[8] Gault and Klees, *Bull. soc. chim.*, **39**, 883 (1926).

[9] Ref. 8, p. 904.

[10] Gault and Klees, *Bull. soc. chim.*, **39**, 1000 (1926).

also a liquid ester were obtained, but each of these products showed only 0.3% enol content by the bromine titration. We have therefore concluded, in agreement with Gault and Klees, that the solid, m. p. 34°, is the almost homogeneous ketonic form of the compound. However, from our experiments, the liquid obtained from this solid by melting, or by liberation from the sodium enolate under the conditions described, also appears to be mainly the ketonic form, *i. e.*, an equilibrium mixture consisting of 99.7% keto and 0.3% enol. In its behavior toward bromine, ferric chloride, phenylhydrazine and semicarbazide acetate, the liquid product shows identical reactions as the solid ester. This is contrary to the observations of Gault and Klees, who stated that their liquid enol form did not react with phenylhydrazine or semicarbazide acetate. Such behavior would be unusual in compounds of this enolic type, and we have not been able to confirm their statement.

Claisen[11] concluded from experimental results obtained from a study of desmotropes that the "tendency towards formation of the hydroxyl form increases with the negativity and the number of the acyl radicals that are adjoined to the methane carbon." As a salient example of the rule, the increase in enolization on passing from tribenzoyl- to dibenzoylacetyl- and then to benzoyldiacetyl-methane was emphasized. This rule was generally accepted until Michael[12] called attention to the curious mistake of Claisen in accepting, contrary to the true relationship, a greater relative negativity for acetyl than for benzoyl. It was also pointed out that the increased stability of the keto form in passing from dibenzoyl- to tribenzoylmethane, and other facts, showed that, in general, the phenomenon with reference to positive and negative influence at the central carbon atom is of a periodic character. The later results of K. H. Meyer[13] and Dieckmann[14] confirmed the view that the rule, in the form stated by Claisen, is not tenable.[15] However, Auwers and Jacobsen[16] observed that the enol content of a number of mono-acylmalonic esters increased in a direct relation to the dissociation constants ($K$) of the aliphatic acids corresponding to the acyl radicals. This is the only group of desmotropes known in which the "Claisen rule" has been shown to be valid, and the connection here is to be attributed to the strictly comparable structures of the members of the group, and the very slight changes in the relative negativity of the acyl groups.

The extent of enolization in acetosuccinic ester compared with those of

[11] Claisen, *Ann.*, **291**, 37 (1898); *Ber.*, **36**, 3674 (1903).

[12] Michael, *Ann.*, **363**, 241 (1908).

[13] Meyer, *Ber.*, **45**, 2849 (1912).

[14] Dieckmann, *ibid.*, **55**, 2470 (1922).

[15] Notwithstanding, it is still quoted as valid in some recent textbooks; *e. g.*, Schmidt. "Lehrbuch der organische Chemie," 1929, p. 259.

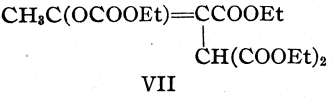
[16] Auwers and Jacobsen, *Ann.*, **426**, 179 (1921).

structurally analogous compounds may serve as a further contribution to this problem:

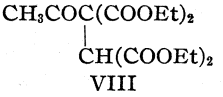
| | | % of enol content |
|---|---|---|
| I | Acetoacetic ester | 7.7 |
| | Acetosuccinic ester[13] | 3.6 |
| | α-Aceto-α′-carbethoxysuccinic ester | 0.3 |
| | α-Aceto-α′,α′-dicarbethoxy succinic ester | 0.0 |
| II | α-Methyl acetoacetic ester | 4.1 |
| | α-Ethyl acetoacetic ester[13] | 3.0 |

From the table it is apparent that the equilibrium relations in the acetosuccinic series do not support the "Claisen rule." Actually, with increasing substitution of α-H by the weakly negative COOEt group, the proportion of the enol form is lowered, instead of increased, as it should be from the "Claisen rule." Since it is also true from II that substitution of H by positive alkyl groups affects the equilibrium in the same direction, it may be concluded that the rule may even be untenable among members with closely comparable chemical structures.

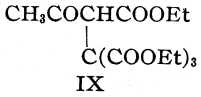
The sodium enolates (III), (IV) and (V) with chlorocarbonic ester should give the carbethoxyl derivatives (VII), (VIII) and (IX), respectively.



VII

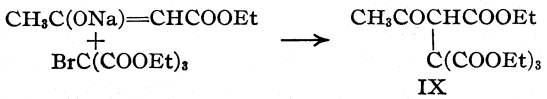


VIII



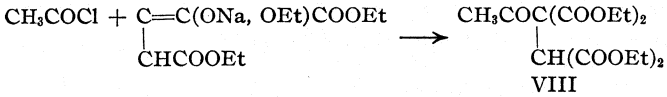
IX

Treatment of the sodium derivative of α-aceto-α-carbethoxysuccinic ester (I) in alcoholic solution with chlorocarbonic ester gave a liquid ester that corresponded to structure (IX) in its reactions. With phenylhydrazine in ether solution it gave a phenylhydrazone identical with the phenylhydrazone of α-aceto-α′,α′-dicarboxysuccinic ester. α-Aceto-α′,α′-dicarbethoxysuccinic ester was also prepared by the action of bromomethanetricarboxylic ester upon sodium enol acetoacetic ester



IX

For comparison, α-acetyl-α,α′-dicarbethoxysuccinic ester (VIII) was prepared by the action of acetyl chloride upon sodium enol ethanetetracarboxylic ester



VIII

When the ester (VIII) was treated with phenylhydrazine in ether solution, it reacted immediately to give β-acetylphenylhydrazide and ethanetetracarboxylic ester in quantitative yield

$$\begin{array}{l} CH_3COC(COOEt)_2 \\ \quad\quad | \\ \quad\quad CH(COOEt)_2 \end{array} + C_6H_5NHNH_2 \longrightarrow CH_3CONHNHC_6H_5 + \begin{array}{l} CH(COOEt)_2 \\ \quad\quad | \\ \quad\quad CH(COOEt)_2 \end{array}$$

Auwers and Auffenberg[3] found that acetylmalonic ester in pyridine solution when treated with chlorocarbonic ester gave a good yield of the O-carbethoxyl derivative. Using the same conditions, $\alpha$-aceto-$\alpha'$-carbethoxysuccinic ester (I) in pyridine solution with chlorocarbonic ester gave a liquid product, b. p. 182–184° (2 mm.), which was apparently a mixture of the O-derivative (VII) with the C-derivative (IX) of the ester in about equal proportion. Upon treatment in ether solution with phenylhydrazine, there were obtained the phenylhydrazones of $\alpha$-aceto-$\alpha'$-carbethoxysuccinic ester and of $\alpha$-aceto-$\alpha',\alpha'$-dicarbethoxysuccinic ester, together with some $\beta$-phenylhydrazine carboxylic ester. O-carbethoxy-$\alpha$-acetyl-$\alpha'$-carbethoxysuccinic ester (VII) should be reacted upon by phenylhydrazine as follows:

$$\begin{array}{l} CH_3C(OCOOEt)=CCOOEt \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad CH(COOEt)_2 \end{array} + 2C_6H_5NHNH_2 \longrightarrow \begin{array}{l} CH_3C—CHCOOE \\ \quad\quad\quad\quad\quad\

$C_6H_5C(OH)=CHCOCH_3$ and $C_6H_5COCH=C(OH)CH_3$ in benzoylacetone undergo reductions to isomeric keto-carbinols and these are further reduced to the glycol derivative. It seemed of interest to examine the behavior of other O-acyl ester derivatives toward this catalytic reduction. Since these experiments were made, the results obtained with several compounds of this character have been published by Roll and Adams.[17] Using acetic acid as a solvent, these chemists showed that O-acetoacetoacetic ester ($\beta$-acetoxycrotonic ester) by catalytic reduction with platinum oxide and hydrogen gave butyric ester, and that O-acetylbenzoylacetone yielded phenyl propyl ketone. This course of reduction with the O-acetyl compounds corresponds with that of O-carbethoxylbenzoylacetone.

We found that with O-carbethoxyacetoacetic ester in methyl alcohol, one molecular equivalent of hydrogen was rapidly absorbed and then about one-half a molecular equivalent of gas was more slowly absorbed. A product was obtained which upon examination proved to be butyric ester. The course of reaction would appear to be analogous to the reduction, under similar conditions, of O-carbethoxybenzoylacetone

$$CH_3C(OCOOEt)=CHCOOEt \xrightarrow{H_2} [CH_3CH(OCOOEt)-CH_2COOEt] \xrightarrow{H_2} CH_3CH_2CH_2COOEt + HOCOOEt$$

Liberation of carbon dioxide as gas from the decomposition of the acid carbonic ester would make the apparent volume of absorption less than two molecular equivalents of hydrogen.

The so-called diacetomalonic ester, shown by Michael[18] and later also by Auwers and Auffenberg,[19] to be O-aceto-enol-acetomalonic ester, or $\beta$-acetoxy-ethylidenemalonic ester, by analogy to the behavior of the O-carbethoxyl- and the O-acetylacetoacetic esters toward reduction, should lead to ethylidene or to ethylmalonic esters, respectively. Experiment showed, however, that this ester in methyl alcohol solution underwent no reduction by molecular hydrogen in the presence of platinum oxide. O-Carbethoxyacetomalonic ester, prepared by the action of chlorocarbonic ester upon sodium enol acetomalonic ester, gave indications of a slow reduction under these conditions. Scholl and Egerer[20] obtained an acetyl derivative by the action of acetyl chloride upon sodium enol methanetricarboxylic ester, to which they ascribed the C-acetyl formula, and the conclusion was verified by Auwers and Auffenberg.[21] We noticed no reduction of this keto derivative under the conditions described above. Likewise, methanetetracarboxylic ester[20] underwent no change.

[17] Roll and Adams, THIS JOURNAL, **53**, 3469 (1931).

[18] Michael, *Am. Chem. J.*, **14**, 495 (1892); *Ber.*, **38**, 2086 (1905).

[19] Auwers and Auffenberg, *ibid.*, **50**, 929 (1917).

[20] Scholl and Egerer, *Ann.*, **397**, 301 (1913).

[21] Auwers and Auffenberg, *Ber.*, **51**, 1087 (1918).

This catalytic hydrogenation, therefore, is not a general test to distinguish between O- and C-acyl derivatives. The protection of the —C(OCOOEt)-=C— group of O-carbethoxyacetomalonic ester, in contrast to the facile reduction of the group in O-carbethoxyacetoacetic ester, must be ascribed to the accumulation of the influence of negative groups at the ethylenic carbon atoms. It results, in the first compound, from the introduction of the negative carbethoxyl group in the place of an H atom of the O-carbethoxyacetoacetic ester. The facility of reduction depends mainly on the free chemical energy at the unsaturated carbons and their affinity for hydrogen. The first condition should be increased by negative influence, while the second should be decreased. Negative chemical influence, therefore, lowers the affinity between the unsaturated C and the H and increases the free chemical energy at the carbon, and, up to a certain balance between these energy factors, the facility of reduction increases; beyond this it begins to fall off. The negative influence, as in O-acetoenol-acetomalonic ester, may become so great that the unsaturated carbons are protected against a mild reducing agent. Positive alkyl groups in the place of an H joined to the unsaturated C of an ethylenic compound depresses both the above energy factors. Hence, the facility of catalytic reduction is progressively lowered with increment of this positive influence at the unsaturated carbon group. For example, Vavon and Kleiner[22] showed that the facility of catalytic reduction (using platinum black) of the following heptenes decreased in the order

$n$-$C_3H_7CH{=}CHC_2H_5$ $CH_3CH{=}C(C_2H_5)_2$ $(CH_3)_2C{=}CHCH(CH_3)_2$ $(CH_3)_2C{=}C(CH_3)C_2H_5$

This order of reducibility corresponds to the extent of positive influence at the unsaturated carbon atoms.[23] There can be no doubt that a close relation between the facility of reduction, the structures of the unsaturated derivatives and the chemical potential of the unsaturated carbon atoms for hydrogen, can be established. In a later communication, with the use of a method of catalytic reduction, we hope to prove such a relation experimentally.

## Experimental

**$\alpha$-Acetyl-$\alpha'$-carbethoxysuccinic Ester.**—The preparation of this ester from chloromalonic and sodium enol-acetoacetic esters as a liquid has been described previously.[7,8] Upon keeping for a day at −10°, the liquid, b. p. 147° (5 mm.), solidified to a solid mass which was recrystallized from ligroin. Needles, m. p. 34°, were obtained, undoubtedly identical with the solid substance described by Gault and Klees.[10] Crystallization of the crude product from ligroin is a ready method of purifying the ester from the cyclic and other keto esters which are also formed in the reaction.

*Anal.* Calcd. for $C_{13}H_{20}O_7$: C, 54.16; H, 6.94. Found: C, 53.98; H, 7.10.

[22] Vavon and Kleiner, *Compt. rend.*, **177**, 401 (1923).

[23] Michael, *J. prakt. Chem.*, [2] **60**, 432 (1899).

A determination of the enol content in methyl alcohol solution by the indirect bromine titration method[24] indicated the presence of 0.3% of enol. After fractional distillation, in the presence of a small amount of phthalic acid, from a Pyrex glass vessel, the enol content rose to 1.6% as the maximum in the fractions. These results confirm the observations of Gault and Klees upon the very small extent of bromine addition shown by this ester.

A solution of 8.7 g. of ester in excess caustic soda (1.5 times the theoretical of 5% solution) at −10° was slowly acidified with the theoretical amount of cold, dilute sulfuric acid (5%). After several minutes, large needle-like crystals (5.0 g.) separated, which were found to be identical with the original ester. The filtrate was rapidly extracted with ether and the solvent removed in a vacuum desiccator. A liquid residue (2.5 g.) was obtained which was proved by titration to be 0.3% enolic. Upon cooling and seeding, it solidified to the solid ester.

The solid ester, m. p. 34°, with alcoholic ferric chloride after several seconds gives a reddish-purple color which fades within a few minutes.

It is evident from these experiments that the ester exists almost entirely in the ketonic form and that the pure enolic form is an exceedingly labile compound, even at temperatures below zero.

An ether solution of 2.8 g. of the ester and 1.1 g. of phenylhydrazine, after standing for two days, gave the phenylhydrazone. This crystallized from ethyl acetate as large needles, m. p. 91° (Gault and Klees[10] gave m. p. 89°).

*Anal.* Calcd. for $C_{19}H_{26}O_6N_2$: C, 60.31; H, 6.88. Found: C, 59.95; H, 7.06.

**Action of Chlorocarbonic Ester upon Sodium Enol-α-acetyl-α′-carbethoxysuccinic Ester.**—To a cold solution of 2.3 g. of sodium in 35 cc. of absolute alcohol, 28.8 g. of ester was added, and then, after thirty minutes, 11 g. of chlorocarbonic ester diluted with ether. After standing for four hours, the mixture was acidified with dilute acetic acid, extracted with ether, the extract washed with aqueous sodium carbonate, dried and the neutral ester distilled under reduced pressure. Some lower boiling liquid was obtained (unchanged ester) but the main product (10 g.) distilled at 182° (2 mm.). The compound gave no color with alcoholic ferric chloride. The analysis indicated that it was a carbethoxyl derivative of α-acetyl-α′-carbethoxysuccinic ester.

*Anal.* Calcd. for $C_{16}H_{24}O_9$: C, 53.34; H, 6.67. Found: C, 53.18; H, 6.9.

When the reaction was carried out in ether solution, a better yield (60%) of this ester was obtained.

An ether solution of 3.6 g. of the ester and 1.1 g. of phenylhydrazine, after standing for several days, gave the phenylhydrazone of α-acetyl-α′,α′-dicarbethoxysuccinic ester, m. p. 104°. Identity was shown by direct comparison and mixed melting point.

*Anal.* Calcd. for $C_{22}H_{30}O_8N_2$: C, 58.67; H, 6.66. Found: C, 58.35; H, 6.92.

**Action of Chlorocarbonic Ester upon α-Acetyl-α′-carbethoxysuccinic Ester in Presence of Pyridine.**—To a solution of 14.4 g. of α-acetyl-α′-carbethoxysuccinic ester in 10 g. of pyridine, cooled in ice water, 6 g. of chlorocarbonic ester was slowly added with rapid shaking. After standing for twelve hours in the cold, ether was added to the semi-solid mass and the pyridine hydrochloride filtered off. After removal of the ether, the residue was distilled under reduced pressure and, besides the lower-boiling fraction (about 4 g.) of unchanged ester, the main fraction (10 g.), b. p. 182–184° (2 mm.), distilled as a colorless liquid.

*Anal.* Calcd. for $C_{16}H_{24}O_9$: C, 53.34; H, 6.67. Found: C, 53.22; H, 6.71.

**Action of Phenylhydrazine.**—To an ethereal solution of this ester, 2.2 g. of phenylhydrazine was added. After standing for two days, large needle-like crystals (1.5 g.)

[24] Meyer and Kappelmeier, *Ber.*, **44**, 2718 (1911).

of the phenylhydrazone of α-acetyl-α′-carbethoxysuccinic ester (m. p. 91°) had separated, which were filtered off and washed with ligroin. The mother liquor was evaporated in a vacuum desiccator and the residue rubbed with carbon disulfide. The deposit of crystals of the phenylhydrazone (m. p. 104°) of α-acetyl-α′,α′-dicarbethoxysuccinic ester (1.0 g.) was filtered off and washed with ligroin and carbon disulfide. The residue in the mother liquor on evaporation in the desiccator and rubbing with ligroin slowly crystallized. The crystals (m. p. 80°) were shown to be identical with β-phenylhydrazinecarboxylic ester.

**α-Acetyl-α,α′-dicarbethoxysuccinic Ester** (Acetyl-*sym.*-ethanetetracarboxylic Ester).—To a suspension in ether of 2.3 g. of pulverized sodium, an ether solution of 32 g. of *sym.*-ethanetetracarboxylic ester was added and the mixture heated on a water-bath until all the sodium had been converted into the sodium derivative. To the cooled mixture, 10 g. of acetyl chloride was added and, after reaction had ceased, it was warmed for an hour. The ether solution was then cooled, washed with dilute acetic acid, followed by aqueous sodium carbonate, dried and fractionated. Two main fractions were obtained: (a) b. p. 160–165° (2 mm.) (17 g.) solidified on cooling and was unchanged ethanetetracarboxylic ester; (b) b. p. 175° (2 mm.) (17 g.) remained a thick liquid and was the mono-acetyl derivative of ethanetetracarboxylic ester. It gave no color with alcoholic ferric chloride and was not reduced by hydrogen in presence of platinum oxide.

*Anal.* Calcd. for $C_{16}H_{24}O_9$: C, 53.34; H, 6.67. Found: C, 53.48; H, 6.46.

**Action of Phenylhydrazine.**—To an ether solution of 1.8 g. of the ester, 0.55 g. of phenylhydrazine was added. There was an immediate reaction and crystals of flat needles separated. After several hours, the mixture was filtered and the crystals washed with ether. They melted at 131° and proved to be acetylphenylhydrazide. The filtrate upon concentration gave crystals of ethanetetracarboxylic ester (m. p. 76°). The amounts obtained of the product showed that the reaction proceeded approximately quantitatively.

**α-Acetyl-α′,α′-dicarbethoxysuccinic ester** was prepared by the action of bromomethanetricarboxylic ester upon sodium enolacetoacetic ester.

To 4.6 g. of pulverized sodium, covered with ether, 26 g. of acetoacetic ester was added. When the formation of sodium enol acetoacetic ester was complete, 62 g. of bromomethanetricarboxylic ester, b. p. 147° (2 mm.),[25] was added and the mixture left to stand for twelve hours. The gelatinous mass was then acidified with dilute acetic acid, and the ether solution washed with aqueous sodium carbonate, dried and the neutral ester fractionally distilled under reduced pressure. A large fraction, boiling up to 150° (2 mm.), contained mainly unchanged material. The fraction boiling between 170–190° (2 mm.) was redistilled and 15 g. of colorless liquid, b. p. 182–184° (2 mm.), was obtained.

*Anal.* Calcd. for $C_{16}H_{24}O_9$: C, 53.34; H, 6.67. Found: C, 53.16; H, 6.82.

This ester slowly gave a faint purple color with alcoholic ferric chloride which faded after several minutes. Indirect titration in methyl alcohol solution with bromine gave no indication of the presence of the enol compound.

**Action of Phenylhydrazine.**—An ether solution of 3.6 g. of the ester with 1.1 g. of phenylhydrazine was permitted to stand for two days. No solid separated so the solution was evaporated in a desiccator and the residue rubbed with carbon disulfide. A fine crystalline powder was formed which was filtered off (2.0 g.). This phenylhydrazone derivative was recrystallized from a mixture of carbon disulfide and methyl acetate and separated as fine needles, m. p. 104°.

*Anal.* Calcd. for $C_{22}H_{30}O_8N_2$: C, 58.67; H, 6.66. Found: C, 58.45; H, 6.76.

[25] Wheeler and Johnson, THIS JOURNAL, **24**, 687 (1902).

**Reduction Experiments with Hydrogen in the Presence of Platinum Oxide.** (a) **O-Carbethoxyacetoacetic Ester.**—To a solution of 2.0 g. of this ester, b. p. 140° (2 mm.), in 50 cc. of methyl alcohol, 0.05 g. of platinum oxide catalyst was added and the mixture shaken in an atmosphere of hydrogen; 230 cc. of hydrogen (N. T. P.) was first absorbed at an average rate of 30 cc. per minute, and then a further 130 cc. of gas were taken up during one hour. The solution was filtered, shaken with activated charcoal and distilled. The product from an experiment using 8.2 g. of ester in 50 cc. of methyl alcohol was combined with the above material. The alcohol solution of the ester produced was distilled up a 20-cm. Vigreux fractionating column. It was found that the ester had completely volatilized in the methyl alcohol. Therefore, the distillate was mixed with 25 cc. of 10% caustic soda and the alcohol slowly distilled off, leaving the aqueous solution of sodium salt. The acid obtained upon acidifying the sodium salt was converted into the acid chloride by treating with thionyl chloride, and this when treated with aniline, gave an anilide, m. p. 96°, which was found to be identical with butyric anilide.

(b) **O-Carbethoxylacetomalonic ester** was prepared by the action of chlorocarbonic ester upon acetomalonic ester in the presence of pyridine, as described by Auwers and Auffenberg.[3] The acetomalonic ester was prepared by action of chlorocarbonic ester upon copper acetoacetic ester.[26] A methyl alcohol solution (50 cc.) of 2.7 g. of this ester with 0.1 g. of platinum oxide absorbed 50 cc. of hydrogen in three hours. (Theory requires 233 cc. for one molecular equivalent of hydrogen.)

(c) **O-Acetylacetomalonic ester** was prepared by method of Michael[18] by the action of acetyl chloride upon sodium enol acetomalonic ester in ether.

(d) **Acetylmethanetricarboxylic ester** was prepared by the method of Scholl and Egerer[20] by the action of acetyl chloride upon sodium enolmethane tricarboxylic ester.

(e) **Methanetetracarboxylic ester** was prepared by the action of chlorocarbonic ester upon sodium enol-methanetricarboxylic ester.[20]

These last three compounds were treated similarly in methyl alcohol solution with hydrogen in presence of the platinum oxide catalyst, but in no case did absorption of hydrogen occur.

## Summary

1. The action of chlorocarbonic ester upon sodium enol $\alpha$-aceto-$\alpha'$-carbethoxy succinic ester has been examined.

2. The results further demonstrated the greater reaction velocity of the sodium enol malonic ester group as compared with the sodium enol acetoacetic ester group, which again is shown to be a function of the degree of neutralization of the reactive element (sodium) in that group.

3. The enol contents of $\alpha$-aceto-$\alpha'$-carbethoxysuccinic and $\alpha$-acetyl-$\alpha,'\alpha'$-dicarbethoxysuccinic esters have been determined and the variation in enolization in these, and in similarly constituted, esters is shown to be opposed to the "Claisen rule."

4. The action of hydrogen in the presence of platinum oxide catalyst upon O-carbethoxyacetoacetic ester, O-carbethoxyacetomalonic ester, O-acetylacetomalonic ester, acetylmethanetricarboxylic ester and methanetetracarboxylic ester has been studied, and it has been found that with increase in the number of the acyl groups about the ethylenic carbon atoms, reduction proceeds with difficulty or not at all.

[26] Nef, *Ann.*, **266**, 105 (1891).

5. The facility of catalytic reduction of ethylenic compounds with reference to chemical structure is discussed.

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## NOTES

**Identity of Neonicotine and the Alkaloid Anabasine.**—In a recent article[1] Orechoff and Menschikoff reported the results of a study of the alkaloids of *Anabasis aphylla L.* (Fam. Chenopodiaceae). The alkaloids isolated and identified were lupinine and anabasine. Anabasine was shown to be β-pyridyl-α′-piperidine. They considered it to be different from nicotimine, an alkaloid associated with nicotine in the tobacco plant, to which Pictet had erroneously assigned this structure.

The writer obtained a sample of "anabasine sulfate" through the courtesy of the Amtorg Trading Corporation and made an examination of the alkaloids. Anabasine was separated and purified. It was found to be identical with neonicotine, the isolation of which the writer reported at the 79th meeting of the Society on April 8, 1930. The report was published on January 12, 1931.[2] Anabasine differs from neonicotine in being levorotatory, whereas synthetic neonicotine is inactive.

The writer isolated neonicotine from the reaction products of sodium, pyridine and oxygen, while he was attempting to separate the insecticidal substance (neonicotine) from the comparatively non-toxic dipyridyls. Although previous workers had reported the presence of isonicotine (γ-pyridyl-γ′-piperidine) in the products of the sodium–pyridine reaction, the writer has been unable to find that any pyridylpiperidine other than neonicotine or β-pyridyl-α′-piperidine[2] is produced in his modified procedure. It is interesting that out of nine compounds theoretically possible, the particular pyridylpiperidine which most closely resembles nicotine should be found in nature. It represents the first dipyridyl alkaloid. It is also interesting to note that this is a rare instance of the synthesis of an alkaloid preceding its isolation from a plant.

In addition to neonicotine the writer found considerable methylneonicotine (methylanabasine) in his sample of anabasine sulfate. Orechoff and Menschikoff do not report this alkaloid as one of the constituents of the *Anabasis aphylla.* When the total mixed alkaloids are dissolved in water and extracted with ether, the anabasine remains in the water, and the methylanabasine is extracted. Its presence was immediately suspected because the ether fraction when evaporated was found to be more soluble in cold water than in hot water, which is generally true of all N-methylpyridylpiperidines.

[1] Orechoff and Menschikoff, *Ber.*, **64**, 266 (1931).

[2] C. R. Smith, THIS JOURNAL, **53**, 277 (1931).

Owing to lack of information of the previous treatment of this sample of "anabasine sulfate" only a brief outline of the work done to establish the identity of neonicotine and anabasine and the presence of methylneonicotine is submitted. It is hoped that a separation of these substances into their optically active forms can be made later.

The total alkaloids were liberated by strong potash solution and extracted with ether. After the ether solution was dried over potash, the ether was removed by evaporation, and the alkaloids were distilled in a vacuum to remove residual tarry bases. The distilled bases were dissolved in water and extracted with ether to remove the methylanabasine fraction. The water solution was acidified with dilute hydrochloric acid, and sodium nitrite was added to form the nitrosoanabasine. This was extracted with ether and decomposed with dilute hydrochloric acid. The anabasine was freed with alkali and extracted with ether. After one or two distillations in a vacuum to remove traces of water and solvent, the anabasine distilled between 277.5 to 280° at 760 mm. The boiling point of neonicotine was given as 280–282° at 775 mm. The picrate was prepared first from alcoholic solutions of the base and picric acid. It was twice recrystallized from water, from which it separated in long needles which melted at 212–214° (Orechoff and Menschikoff report an indefinite melting point of 200–205°, presumably corrected). Neonicotine picrate melts at 213°. When it was mixed with the anabasine picrate it showed some softening at 208° but melted at 212°. Orechoff and Menschikoff proved the identity of anabasine through the formation of nicotinic acid by alkaline permanganate and the formation of $\alpha,\beta'$-dipyridyl by dehydrogenation with zinc dust. Their description of the picrate of their dipyridyl exactly duplicates results previously observed by the author for pure $\alpha,\beta'$-pyridyl and leaves no doubt as to the correctness of their conclusion.

The author has found that pure anabasine when hydrogenated takes up nearly the theoretical amount of hydrogen and forms a dipiperidyl boiling at 269°. The dipiperidyl was first separated from alcoholic solution as the crystalline dihydrochloride, from which the base was liberated by alkali. Since the anabasine dipiperidyl would also be optically active, the picrate and the dinitroso derivatives would be expected to be different from those of the synthetic $\alpha,\beta'$-dipiperidyl. The picrate, however, was found to melt at 224° which was not appreciably lowered when the synthetic dipiperidyl picrate was added. The dinitrosodipiperidyl obtained from anabasine, however, melted at 111–112° while the synthetic melts at 88°; a mixture of the two softened below 75° but no definite melting point could be obtained. The author has not attempted the resolution of $\alpha,\beta'$-dipiperidyl so that no exact comparison could be made.

In the writer's first study of the oxidation of neonicotine with permanganate, nicotinic acid was not obtained, but a repetition of the oxidation

using alkaline permanganate showed a smooth oxidation to nicotinic acid. As the chief impurity in the earlier preparations of neonicotine was β,γ-dipyridyl, which might also have produced nicotinic acid, little attention was paid to the oxidation.

The methylanabasine fraction was distilled several times, but only the fraction from 270 to 275° was collected. The picrate was formed in fine needles which softened at 215° and melted at 222–223° (corr.) with gas evolution. Some anabasine was methylated by treatment with potassium methyl sulfate, and a picrate was prepared which softened at 217° and melted at 222–223°. When the two were mixed the melting point was 219–220°. Because of the slight differences in the boiling point of the bases and the melting point of their picrates, an optical study was made by Mr. George L. Keenan.

**Anabasine Picrate, Natural.**—This material consists of yellow, plate-like rods, usually six-sided in outline. In parallel polarized light (crossed nicols), the extinction usually is straight and occasionally inclined. In convergent polarized light (crossed nicols), a biaxial interference figure with the optic axis up or slightly inclined is occasionally seen. The most significant refractive index determinable by the immersion method was the minimum value, $n_\alpha$ 1.585, frequently shown on irregular fragments and lengthwise on the elongated forms; $n_\beta$ and $n_\gamma$ were found to be considerably higher than the refractive index for methylene iodide.

**Neonicotine Picrate.**—The optical crystallographic data for this substance were found to be identical with those obtained for natural anabasine picrate.

**Picrate of the Natural Anabasine, Methylated.**—This substance crystallizes in small, yellow needles. In parallel polarized light (crossed nicols), the extinction is straight. Biaxial interference figures are rarely seen with convergent polarized light (crossed nicols). The minimum refractive index, $n_\alpha$ 1.616, is very common on irregular fragments and on the elongated forms lengthwise; $n_\beta$ and $n_\gamma$ are considerably higher than the refractive index for methylene iodide.

**Picrate of the Natural Methyl Anabasine.**—This was found to be identical with the previous picrate in so far as optical crystallographic data are concerned.

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**Bromomethyl Normal Alkyl Ethers.**—Although many investigators have utilized Henry's method[1] for the preparation of α-halogenated ethers to obtain the chloro compounds, the synthesis of the corresponding bromo derivatives has received but scant attention and the preparation and physical properties of only the methyl,[2,3] ethyl[3] and *n*-propyl-[3] ethers

[1] L. Henry, *Bull. soc. chim.*, **44**, 458–459 (1885); *Compt. rend.*, **100**, 1007–1009 (1885).

[2] L. Henry, *Bull. acad. roy. Belgique*, [3] **25**, 439–440 (through *Ber.*, **26**, ref. 933–934 (1893).

[3] A. Karvonen, *Ann. Acad. Sci. Fenn.*, (A) 5, **6**, 109 (through Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. 1, Supplement 1, p. 305).

have been described in the literature. It is the purpose of this note to record the preparation of the *n*-butyl and *n*-amyl ethers and to correct the erroneous value reported for the index of refraction of the *n*-propyl ether.

**Experimental.**—A stream of hydrogen bromide gas[4] was passed into a well-cooled mixture of 75 cc. of aqueous formaldehyde solution and one mole of the appropriate alcohol until saturation occurred with resulting separation of the mixture into two layers. The upper layer was then separated and dried over calcium chloride for at least two hours. Most of the excess hydrogen bromide was removed by placing the ether under a partial vacuum and drawing a small stream of dry air through it, but complete removal of the gas was accomplished only by treating the ether with anhydrous potassium carbonate. Distillation of the crude ether at atmorpheric pressure resulted in profound decomposition. However, by maintaining a pressure below 20 mm. it was possible to purify the ethers by fractional distillation. Our experience in purifying these ethers indicates that as the molecular weight increases the stability of these compounds, as indicated by the ease of hydrolysis, markedly decreases. The properties of the ethers synthesized in this investigation are given in Tables I and II.

TABLE I

BROMOMETHYL *n*-ALKYL ETHERS, $CH_2Br—O—R$

| R- | Yield, % | $d_4^{20}$ | $n_D^{20}$ | Molecular refraction Calcd. | Molecular refraction Found | Analyses, Br % Calcd. | Analyses, Br % Found | Molecular wts. Calcd. | Molecular wts. Found |
|---|---|---|---|---|---|---|---|---|---|
| *n*-Propyl | 80 | 1.3551 | 1.4515 | 29.89 | 30.32 | 52.22 | 52.38 | 153.0 | 155.1 |
| *n*-Butyl | 78 | 1.2702 | 1.4514 | 34.48 | 35.35 | 47.88 | 47.87 | 167.0 | 171.3 |
| *n*-Amyl | 99 | 1.2129 | 1.4512 | 39.07 | 40.11 | 44.14 | 43.49 | 181.0 | 185.5 |

TABLE II

BOILING POINTS

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Bromomethyl *n*-Propyl Ether | | | | | | | | |
| *T*, °C. (corr.).... | 48 | 54.6 | 62.5 | 71.6 | 84.0 | 98.0 | 133.3 | |
| *P*, mm..... | 20 | 31 | 49 | 73 | 125 | 210 | 747.5 | |
| Bromomethyl *n*-Butyl Ether | | | | | | | | |
| *T*, °C. (corr.) | 57.2 | 65.7 | 73.2 | 80.8 | 85.6 | 90.3 | 101.0 | 108.2 | 159.0 |
| *P*, mm..... | 20 | 30 | 45 | 62.5 | 76 | 97 | 137.5 | 170 | 749.5 |
| Bromomethyl *n*-Amyl Ether | | | | | | | | |
| *T*, °C. (corr.). | 71.8 | 83 | 92.2 | 100.7 | 113 | 130.2 | 140.4 | 178–180 (dec.) | |
| *P*, mm..... | 7 | 15 | 28 | 45 | 76 | 150 | 214 | 748.3 | |

From Karvonen's[3] data for the density and index of refraction for the *n*-propyl ether, the molecular refractivity may be calculated to be 30.73.

[4] J. H. Kastle and J. H. Bullock, *Am. Chem. J.*, **18**, 105–111 (1896).

A similar calculation using the data in Table I yields 30.32, which is in closer agreement with the calculated value.

CONTRIBUTION FROM THE
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## COMMUNICATIONS TO THE EDITOR

### THE 4-*n*-ALKYL-GUAIACOLS

*Sir:*

In a recent paper by Coulthard, Marshall and Pyman [*J. Chem. Soc.*, 280 (1931)] on the variation of phenol coefficients, a number of *n*-alkyl guaiacols were prepared and studied. In view of the fact that the latter compounds were under investigation in the authors' laboratory at a much earlier date [Master of Science Thesis submitted by Norine Hower Howells at the Oklahoma A. and M. College, 1929] and since the methods of synthesis were somewhat different, it appears worth while to report briefly the results of this earlier work.

The 4-*n*-alkyl guaiacols were prepared here by the reduction of the corresponding acyl guaiacols, which were obtained after the method of Howells, Little and Andersen [THIS JOURNAL, **52**, 4077 (1930)] by the oxidation of the carbinols resulting through the reaction of the benzoate of vanillin with *n*-alkylmagnesium halides. Unlike the work of Coulthard, Marshall and Pyman, the readily formed solid benzoate ester and diphenyl urethan were selected as derivatives for characterizing the new phenols.

The 4-*n*-pentyl guaiacol (b. p. 156–158° at 20 mm.) which resulted in good yields when 4-*n*-valeryl guaiacol was reduced by the Clemmensen method, was found also to have the maximum phenol coefficient for the series, comparable to the findings of the above authors.

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### INTERMEDIATE PRODUCTS IN THE THERMAL DECOMPOSITION OF AMMONIA

*Sir:*

An attempt has been made to identify the molecule NH as an intermediate product in the thermal decomposition of ammonia, through a study of the absorption spectrum of the decomposing gas. The emission band at λλ 3360–70, long known from photographs of the ammonia–oxygen

[5] This note is taken from a portion of a thesis submitted by Charles M. Blair in partial fulfilment of the requirements for the degree of Master of Arts.

flame, has been ascribed to the NH molecule by Hulthen and Nakamura [*Nature*, **119**, 235 (1927)]. Gaviola and Wood [*Phil. Mag.*, [7] **6**, 1191 (1928)] obtained the band in fluorescence, by the action of excited mercury atoms on a mixture of nitrogen and hydrogen. Recently Bates and Lavin [*Proc. Nat. Acad. Sci.*, **16**, 804 (1930)] were unsuccessful in obtaining this band in absorption from the active products issuing from a discharge in ammonia. They concluded, however, from a chemical study that the gas contained either NH or $NH_2$.

Since it is possible that NH molecules formed on a surface may be unable to leave as free radicals, the attempt was made to obtain light absorption by the molecules on the surface in the following way: continuous ultraviolet radiation from a hydrogen discharge was focused, at a slight angle, at the end of a highly polished platinum tube whose ends were sealed into soft glass tubes furnished with plane quartz windows. The light suffered multiple reflections within the tube, and that coming out was focused on the slit of a Hilger quartz spectrograph. Ammonia was passed at a slow rate through the tube at atmospheric pressure in some experiments; in others the tube was filled with ammonia at various pressures and the rate measured simultaneously in a static system. The temperatures used were from 800 to 1125°.

Absorption in the region 3360 Å. could not be found on any of the plates. The absorption bands of ammonia from 2260 Å. to about 1900 Å. appeared very strong in all photographs taken at temperatures below 800° even at 20 mm. pressure. Above 800° these gradually disappeared, until at 1125° no trace remained. A few new weak bands, not previously reported, appeared in the region 2300–2450 Å. but were not sufficiently intense for wave length determinations. These may be due, perhaps, to absorption by ammonia in some higher vibrational state. We infer from the weak intensity of ammonia bands and from reaction velocity measurements that almost complete decomposition must have resulted at the higher temperatures. The duration of the absorption measurements was usually one-half hour.

Failure to detect the NH band can be due neither to insufficient decomposition of $NH_3$ nor to a too short life of the NH molecule. In the gas phase it is reported to have a lifetime of $10^{-3}$ seconds, which is longer than the usual lives of adsorbed molecules. Either the surface decomposition does not proceed according to the mechanism $NH_3 = NH + H_2$, or due to a possibly low absorption coefficient our effective absorbing layer was too short.

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## THE CONVERSION OF PARA HYDROGEN TO ORTHO HYDROGEN OVER IRON SYNTHETIC AMMONIA CATALYSTS

*Sir:*

From studies carried out by various authors [Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B,** 113 (1929); A. Farkas, *ibid.*, **10B,** 419 (1930); **14B,** 371 (1931); Bonhoeffer and Farkas, *ibid.*, **12B,** 231 (1931); Taylor and Sherman, THIS JOURNAL, **53,** 1614 (1931)] it has generally been concluded that hydrogen becomes "activated" during its conversion on metallic surfaces from the para to the ortho form. This "activation" on tungsten and platinum in particular has been interpreted as a surface dissociation into adsorbed hydrogen atoms [Bonhoeffer and Farkas, and Farkas, *loc. cit.*]. In continuing the study that this Laboratory has been making of the mechanism of the catalytic synthesis of ammonia, it has seemed worth while to determine the conditions under which hydrogen molecules on iron synthetic ammonia catalysts become sufficiently activated to bring about the para–ortho conversion and to compare the rates of this conversion to the known rates of ammonia synthesis on the same catalysts.

The only references heretofore made to the activity of iron for the para–ortho conversion were by Bonhoeffer and Harteck (*loc. cit.*), who reported coarse iron to be inactive and pyrophoric iron to be capable of effecting only a relatively slow transformation at room temperature, the times of contact of the hydrogen and iron in neither case being specified. The present experiments have been carried out by a flow method, a stream of 49:51 para–ortho hydrogen being passed over 5 cc. of an ammonia catalyst at various temperatures at a rate of flow of 50 cc. per minute. A pure iron catalyst prepared by the reduction in hydrogen at 450–550° of fused $Fe_3O_4$ has been used. It is much less active as an ammonia catalyst than some of the promoted varieties. Nevertheless, at a temperature of 40° it converts a 49:51 para–ortho mixture to a 27.6:72.4 mixture in the very short time of contact accompanying the above-mentioned flow. At −20, 0, 20 and 40°, the percentage conversions from the entering 49:51 to the equilibrium 25:75 mixture are 19, 42, 69 and 89%, respectively.

The extent to which hydrogen must be activated by the catalyst in the catalytic synthesis of ammonia from hydrogen–nitrogen mixtures is not at present known [see Frankenberger's article in Ullman's "Enzyklopädie der Technischen Chemie, 1928]. It is well established, however, that on the catalyst used in the present experiments appreciable rates of ammonia synthesis are not obtained below 300–400°. Accordingly, from the present experiments if one assumes that the activation of hydrogen during its conversion by an iron catalyst from the para to the ortho form is a type that puts it in an active form so far as catalytic hydrogenations in

general are concerned, then one may conclude that the limiting factor in the synthesis of ammonia is not the rate of activation of the hydrogen but the rate at which the nitrogen molecule can be brought into a reactive form by the catalyst.

Benton and White [THIS JOURNAL, **53**, 3301 (1931)] have pointed out that activated adsorption of hydrogen on a sample of this same iron catalyst begins between $-78°$ and about $0°$. The results obtained in the present research seem entirely consistent with their conclusion. The study of the kinetics and temperature coefficient of the para–ortho hydrogen conversion on various synthetic ammonia catalysts is being continued.

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## THE ALLYLIC REARRANGEMENT OF CROTYL BROMIDE AND CROTYLMAGNESIUM BROMIDE

*Sir:*

In view of the recent appearance of an article by Gilman and Harris[1] on the allylic rearrangement of cinnamylmagnesium chloride, it seems advisable to present a preliminary report on the allylic rearrangement of crotylmagnesium bromide.

Using the method of Dillon, Young and Lucas[2] we have analyzed butenes obtained from the following steps: *trans*-crotonaldehyde ⟶ crotyl alcohol ⟶ crotyl bromide ⟶ 2-butene. The 2-butenes obtained by the action of (a) zinc and aqueous alcohol on crotyl bromide and (b) dilute acid on crotylmagnesium bromide, both contained approximately 10% 1-butene. This was contrary to our expectations since crotyl bromide, according to the work of Prévost[3] and Bouis[4] should be free from $\alpha$-methylallyl bromide and thus give pure *trans*-2-butene. The presence of 1-butene in these mixtures must be attributed to an allylic rearrangement of the crotyl bromide or of the Gringard reagent and the corresponding zinc compound. Recent work in this Laboratory on crotyl alcohol and work on 2-pentene-1-ol by Meisenheimer and Link[5] indicates that an allylic transformation probably does occur during the preparation of the bromide. For example, the boiling ranges of different crotyl bromide preparations vary from 1–12° depending on the procedure used.

[1] Gilman and Harris, THIS JOURNAL, **53**, 3541 (1931).
[2] Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).
[3] Prévost, *Ann. chim.*, [10] **10**, 147–181 (1928).
[4] Bouis, *Bull. soc. chim.*, [4] **41**, 1160 (1927).
[5] Meisenheimer and Link, *Ann.*, **479**, 260 (1930).

In order to determine whether or not an allylic transformation also results during the formation of the Grignard reagent, we have converted all of these bromide preparations containing variable quantities of α-methylallyl bromide, into the magnesium compound under identical conditions. The resulting butene mixtures should be of constant composition regardless of the composition of the bromides if an allylic equilibrium is involved; if not, the butene mixtures should have compositions corresponding to those of the bromide preparations. The results of these experiments will be available in the near future.

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ARTHUR N. PRATER

RECEIVED DECEMBER 2, 1931
PUBLISHED JANUARY 7, 1932

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## TESTS FOR ELEMENT 87 (VIRGINIUM) BY THE USE OF ALLISON'S MAGNETO-OPTIC APPARATUS

*Sir:*

In December, 1930, one of us (McGhee) handed out by number to Professor Allison twelve (to him) "unknowns" which were tested by him and checked by two assistants 100% correctly in three hours. The improved model of his machine which was later installed in our laboratory under Dr. Allison's direction has been proved to be reliable by numerous tests on known solutions of pure substances. No two, different, metallic salts of the same acid produce minima that coincide. Hence we read with interest the footnote to an article by Papish and Wainer [THIS JOURNAL, **53**, 3818 (1931)] in which it was suggested that "solutions of $SnCl_4$ and $ReCl_2$ gave minima which were coincident with those obtained for element 87," possibly due to the formation of the complex ions, $SnCl_3^+$ and $ReCl^+$.

To test this question, hydrochloric acid solutions of the minerals samarskite, pollucite and lepidolite, and of crude cesium chloride were made up. Element 87 (Virginium) had been reported in all of them. When observations were made on these solutions within the scale limits between which ViCl would fall, twelve minima were found. Similar observations on the sulfates of the minerals yielded only six minima. Since the same number of minima are always found for any one metal, no matter to which acid radical it might belong, it was thought that six of the minima appearing in the chloride region might indeed be due to $ReCl^+$ and $SnCl_3^+$. With this in view, a solution of pure $SnCl_4$ was made up and examined for minima. In addition to the minima of $SnCl_4$ previously determined, four minima at 44.20, 44.40, 44.98, 46.06 were found. Likewise a solution of $ReCl_2$ (obtained by adding hydrochloric acid to pure potassium perrhenate) was examined for minima. Beside those previously attributed

to $ReCl_2$, minima at 45.93 and 47.54 were observed. The four minima of $SnCl_4$ and the two of $ReCl_2$ which occur at the scale readings given above, coincide with six of those observed in hydrochloric acid solutions of the minerals tested. The other six, which belong to Virginium, occur at 44.01, 44.62, 45.11, 46.22, 46.42, 47.80. *There are no corresponding minima for rhenium and tin in sulfate solutions of these minerals. None of the minima attributed to ViCl was found in the solutions of stannic chloride or rhenium chloride.*

A careful observer need not confuse the minima of Virginium with those of rhenium and tin since the minima of Virginium are in no case nearer than 2.5 cm. to the minima of these elements. In this work each of us has made ninety independent observations, sixty-three of which agree within 1 mm. each with the other; and twenty within 2 mm., while no other variation exceeds 3 mm.

DEPARTMENT OF BIOCHEMISTRY
OF EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA
J. L. MCGHEE
MARGARET LAWRENZ

RECEIVED DECEMBER 2, 1931
PUBLISHED JANUARY 7, 1932

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## DRY DISTILLATION OF COPPER PHTHALATE DOES NOT YIELD FLUORANE

*Sir:*

In THIS JOURNAL, **52**, 3003 (1930), Ekeley and Mattison published a paper entitled "Fluorane from the Dry Distillation of Copper Phthalate." In a recent letter to me (the senior author), L. P. Kyrides of the Monsanto Chemical Works stated that the results as described in the above paper could not be duplicated in his laboratory. I regret to say that I also am unable to duplicate them, the distillate evidently being an impure phthalic anhydride. In 1923 at my suggestion the junior author of the paper performed the experimental work. It never occurred to me to doubt the accuracy of the melting point determinations and the two sets of combustion data as reported by her, since the product she presented dissolved in concentrated sulfuric acid with yellow-green fluorescence. Publication of the results was withheld until similar experiments could be performed on copper tetrachlorophthalate which seemed to point to the formation of dodekachlorofluorane, though analyses by another experimenter no nearer than within 1% of the theoretical were ever obtained. The final responsibility for the publication of the 1923 results on copper phthalate rests upon me, since I should have verified the junior author's data before publication and thus have avoided the erroneous statement appearing in the literature.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO
JOHN B. EKELEY

RECEIVED DECEMBER 22, 1931
PUBLISHED JANUARY 7, 1932

## THE HYDROGEN–CARBON DIOXIDE REACTION

*Sir:*

Smith and Hirst [*Ind. Eng. Chem.*, **22**, 1037 (1930)] observed that hydrogen and carbon dioxide formed carbon monoxide and water over methanol catalysts at atmospheric pressure.

We have been able to confirm this reaction and in addition obtain the regular methanol formation simultaneously using an unsupported zinc–copper–aluminum catalyst under pressure at high temperatures. This catalyst was not particularly active but served as an indication of the course of the reaction. For example, with an initial gas mixture of 27% $CO_2$, 71% $H_2$ and 2% $N_2$ at 325° and 1700 lb. pressure, the effluent gas contained 4% CO and calculations showed an exact agreement with the water found in the condensate compared with the amount produced in the formation of the methanol by the regular reaction.

This suggests that the primary step in the synthesis of methanol from carbon dioxide and hydrogen involves the reduction of carbon dioxide, and the nature of the catalyst determines the extent to which the resultant carbon monoxide will be hydrogenated. Experimental results indicate that as the activity of the catalyst decreases the methanol reaction is most affected, as illustrated by an increase in the carbon monoxide percentage and a decrease in methanol as the catalyst aged. Experiments with this same catalyst using water gas gave appreciable amounts of carbon dioxide in the exit gas.

This observation coupled with the apparent formation of a copper carbonyl during the same reaction suggests a new mechanism for the synthesis of methanol which will be discussed later.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA

E. H. BOOMER
H. E. MORRIS

RECEIVED DECEMBER 23, 1931
PUBLISHED JANUARY 7, 1932

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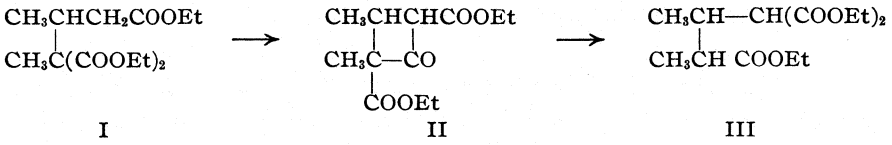
## THE ADDITION OF SODIUM ENOL ALKYLMALONIC ESTER TO BENZALACETOPHENONE

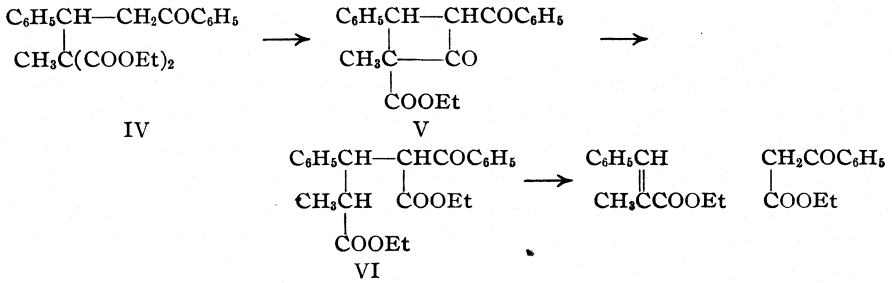
*Sir:*

In a recent communication [Michael and Ross, THIS JOURNAL, **52**, 4598 (1930)] it was shown that addition of sodium enol methylmalonic ester to crotonic ester resulted in a 60% yield of $\alpha,\beta$-dimethyl-$\gamma$-carbethoxyglutaric ester and it was concluded that the methyl group migrated directly in the addition process. Holden and Lapworth [*J. Chem. Soc.*, 2368 (1931)] have suggested that the primary addition compound may be converted into the final product through the intermediate formation and decomposition of the cyclobutanone structure II



I II III

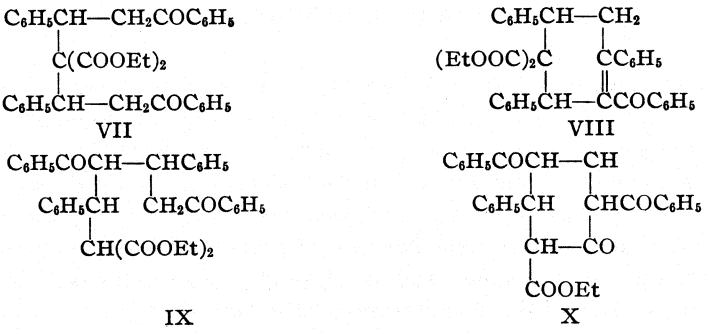
This interpretation involving the formation of a cyclobutanone derivative under these conditions is open to theoretical objections. Holden and Lapworth have based their argument upon their demonstration that treatment of benzalacetophenone (chalcone) with a suspension of sodium enol methylmalonic ester in benzene gives benzoylacetic and $\alpha$-methylcinnamic esters with some high boiling products. By analogy with the above scheme the benzoylacetic and $\alpha$-methylcinnamic esters were considered to be produced by retrogression of the structure VI derived from the tetracyclic ketonic compound V



IV V VI

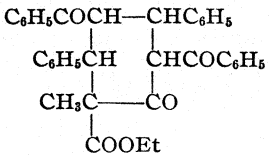
These authors have overlooked the fact that a close parallel does not exist in the addition reactions of crotonic ester and chalcone. The latter compound forms addition products with extraordinary facility [compare Kostanecki and Tambor, *Ber.*, **29,** 1495 (1896)]. Dieckmann and Kron [*Ber.*, **41,** 1277 (1908)] showed that with sodium enol malonic ester a hexacyclic compound IX is produced.

In a reëxamination of the last reaction we have found that two types of compounds are formed which are illustrated by structures VII, VIII, IX and X, respectively

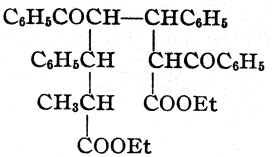


IX X

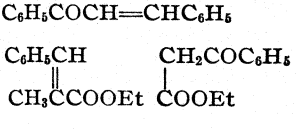
With methylmalonic ester only addition products of the type IX and X can be formed



XI



XII



The ester XI upon treatment with sodium ethoxide in ether solution readily undergoes fission to give benzoylacetic and $\alpha$-methylcinnamic esters and benzalacetophenone, which is in agreement with the results of Dieckmann on the decomposition of open chain and cyclic keto-esters.

Since under the conditions of Holden and Lapworth's experiment, the hexacyclic compound XI could be formed, it is probably the intermediate in the series of reactions which produce $\alpha$-methylcinnamic and benzoylacetic esters. Consequently the obtaining of the latter products cannot be considered as support for their view of the mechanism of this addition reaction.

Corresponding reactions involving one molecule of methylmalonic ester and two molecules of crotonic ester cannot explain the production of $\alpha,\beta$-dimethyl-$\gamma$-carbethoxyglutaric ester in the addition of sodium enol methylmalonic and crotonic esters.

CONVERSE MEMORIAL LABORATORY
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ARTHUR MICHAEL
JOHN ROSS

RECEIVED DECEMBER 24, 1931
PUBLISHED JANUARY 7, 1932

## NEW BOOKS

**André Job. Formes Chimiques de Transition. Oeuvres recueillies par J. Perrin et G. Urbain. (Chemical Forms of Transition. Collected Works by J. Perrin and G. Urbain.)** Hermann et Cie, 6 Rue de la Sorbonne, Paris, France, 1931. xvii + 340 pp. Portrait. Price, fr. 95.

This impressive memorial volume contains a collection of the more important works of André Job. In the first section are the memoirs dealing with problems in theoretical chemistry, and in particular with the mechanism of chemical reaction; in the second section are the memoirs describing experimental investigations. A thoughtful and moving Discourse by Jean Perrin and a Notice on the Life and Works of André Job by Georges Urbain serve as an appropriate introduction.

As is pointed out in the Preface, Job in his diction and style conforms to the French tradition of elegance and brevity. Like the masters of our science whom he admired, Job strove to retain only those results which

counted and those ideas which illuminated. His motto was not "ever more facts" but "ever more light."

In these days when not only our Science but also our Journals are threatened with asphyxiation by the constantly rising tide of uncorrelated facts, should we not give earnest consideration to the mode of presentation so well exemplified by André Job's works?

ARTHUR B. LAMB

**Text-book of Quantitative Analysis.** By WILLIAM THOMAS HALL, Associate Professor of Analytical Chemistry at the Massachusetts Institute of Technology. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1930. vii + 279 pp. 15.5 × 23.5 cm. Price, $2.50.

Teachers who like the methods given in Treadwell–Hall will welcome this text designed for a year's course by Professor Hall. Placing volumetric analysis first will appeal to most people for the reason cited by the author in his preface: ". . . . students accomplish more work, and get more out of the course when this (placing volumetric analysis first) is done." Several of the sections should be amplified in later editions, *e. g.;* the factors governing the choice of indicators (p. 41), co-precipitation phenomena, calculation of the equivalents in oxidation reduction reactions. For a beginning text, it would seem preferable to compel the students to calculate equivalent weights, rather than to give them a table (p. 65). The reason given for not heating sodium bicarbonate above 300° (p. 48) seems inadequate. Sodium carbonate does *not* begin to decompose at 300°; instead, it merely becomes hygroscopic, which leads to low results.

LOUIS WALDBAUER

**A Comprehensive Treatise on Inorganic and Theoretical Chemistry.** By J. W. MELLOR, D.Sc., F.R.S. Vol. XI. Tellurium, Chromium, Molybdenum, Tungsten. Longmans, Green and Co., 55 Fifth Ave., New York, 1931. xii + 909 pp. 221 figs. 16.5 × 25 cm. Price, $20.00.

Tellurium, chromium, molybdenum and tungsten form numerous, multifarious and complicated compounds which stubbornly resist any attempts at simple presentation. They are, speaking anthropomorphically, heterodox and recalcitrant. Nevertheless, the present volume attacks them manfully and with a large measure of success, exhibiting the same clarity and brevity of statement that characterized the earlier volumes of this important encyclopedia of inorganic and theoretical chemistry.

It should be pointed out, however, that even in this exhaustive treatise it has been possible to give only brief summaries of such important classes of substances as the chromium ammines, the tungsten bronzes and the complex acids of molybdenum and tungsten.

ARTHUR B. LAMB

**The Nature of a Gas.** By LEONARD B. LOEB, Professor of Physics, University of California. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1931. x + 153 pp. 11 figs. 15.5 × 23.5 cm. Price, $2.50.

This volume is the first of a series of monographs to be published under the auspices of the Committee on Electrical Insulation of the Division of Engineering and Industrial Research, National Research Council. The reason for this book is that gases are utilized as insulators. It is therefore of importance for student and engineer to understand the structure and electrical properties of gases. Professor Loeb discusses the electron, the proton and their arrangement in atoms and molecules, the structure of molecular spectra, the kinetic theory of gases (in simplified form), ionization phenomena such as critical potentials, single and multiple ionization and their probabilities, and various methods of ionizing gases, in a brief but particularly crisp and lucid manner. A few typographical errors were noted. The work should find many readers in all fields of science and engineering who desire a simple and straightforward account of the fascinating structure and behavior of a gas.

BERNARD LEWIS

**The Structure of Crystals.** By RALPH W. G. WYCKOFF. Second edition. American Chemical Society Monograph. The Chemical Catalog Co., Inc., 419 Fourth Ave., New York, 1931. 497 pp. Illustrated. 15.5 × 23.5 cm. Price, $7.50.

The second edition of this monograph, while similar to the first in its treatment of the subject, has been completely revised. An introductory chapter is followed by a discussion of the symmetry of crystals, the properties of x-rays and their interaction with crystals, and descriptions of methods and apparatus used in crystal analysis. The procedures followed in the determination of crystal structures from x-ray diffraction data are outlined.

The results of crystal analysis are summarized in Part II. The limitation of space necessitated an extremely condensed treatment of the crystal structures of the elements, and of inorganic and organic compounds. The structures are illustrated by projections upon some faces and by spatial arrays of shaded spheres. The results of many incomplete structure determinations and of studies of alloy systems could not be presented. The complete bibliography at the end of the book, however, includes references to such works.

The treatment of the subject is far more lucid than that of the first edition. The discussion of the fundamentally important topic of the interaction of x-rays and crystals, however, is still quite inadequate. The apparatus described while satisfactory is inferior to that used in many European and some American laboratories. The results of crystal structure determinations could scarcely have been presented in a more satisfactorily condensed form. The research worker, however, will find that

this second part in no manner replaces the "Strukturbericht," of P. P. Ewald and C. Hermann ("Structure Review, appearing in the *Zeitschrift für Kristallographie*"). For him the bibliography at the end of the book is its most noteworthy feature.

STERLING B. HENDRICKS

**Lunge and Keane's Technical Methods of Chemical Analysis.** Edited by CHARLES A. KEANE, D.Sc., Ph.D., Formerly Principal of the Sir John Cass Technical Institute, London, and P. C. L. THORNE, M.A., M.Sc., Ph.D., Chief Lecturer in Chemistry, Woolwich Polytechnic. Vol. III. Second edition. D. Van Nostrand Co., 250 Fourth Ave., New York, 1931. xx + 678 pp. Illustrated. 16.5 × 25 cm. Price $18.00.

This third volume of the revised edition of this compendious quantitative analysis is divided into eleven sections with the following subject headings: Clays, Ceramic Products and Refractories—Chemical Examination; Clays, Ceramic Products and Refractories—Physical Examination; Glass; Calcareous Cements; Drinking Water and Water Supplies; Feed Water for Boilers; Sewage and Effluents; Fertilizers; Feeding Stuffs; Soils; Air. Twelve British chemists are listed as contributors, and, in general, they are men prominent in the particular field discussed. The book is written primarily for use in laboratories where British specifications and apparatus are employed, although in several sections references are made to American standards and specifications, and less frequently to those of Germany and France.

Of the 659 pages of the text, 382 are devoted to clay products, glass, and cements. These sections are more complete than in any other treatise of the same nature in English, and should be of value to workers in this field. The remaining sections of the book, especially those on water and sewage, while presenting interesting general information, are concerned with analytical methods, so thoroughly covered by publications of various government laboratories and national associations in America that they cannot be of great value to analytical chemists in this country.

In general, the descriptions of analytical methods are not encumbered with an appreciable number of alternative methods, and few suggestions are offered for the detection and removal or avoidance of the effect of the unusual and unexpected materials frequently found in industrial mixtures. From the standpoint of the average analyst, this is probably a virtue, but those in charge of a control laboratory may be required to look for more detailed guidance. The directions for carrying out the various determinations are clearly written, and the general appearance of the book, with large type and good quality paper, is excellent. It is remarkably free from typographical errors.

As previously indicated, several sections in the book describe analytical

procedures, now considered to be inadequate in this country, and many chemists may feel that the procedures outlined are not only inadequate but that directions for carrying out essential determinations have been omitted. For example, in the sections on water and sewage, no mention is made of methods of determining bio-chemical oxygen demand, $P_H$ by potentiometric instruments, and little mention is made of the widely used color standard comparison methods of the American laboratory.

However, the volume is more than a compilation of analytical methods. The various industrial products, for which analytical methods are presented, are discussed as to source, properties, and effect on the finished product. The book should, therefore, be of value because of this general information which gives the analyst more adequate knowledge of the relation of his work to the industry as a whole.

C. R. HOOVER

**Physical Chemistry. An Elementary Text, Primarily for Biological and Pre-medical Students.** By LOUIS J. GILLESPIE, Ph.D., Professor of Physicochemical Research, Massachusetts Institute of Technology. McGraw-Hill Book Co., Inc., 370 Seventh Ave., New York, 1931. ix + 287 pp. 43 figs. 14.5 × 21 cm. Price, $2.75.

This text-book is planned for students of biology. Special attention is paid to such subjects as surface tension, vapor pressure, the properties of solutions and to applications of the law of mass action. "An attempt has been made to prepare the reader intelligently to consult standard authorities, to bridge the gap between the teaching of elementary principles and the thought and practice of specialists, and, in general, to give him such aid of this sort as is possible without interfering with the presentation of general principles."

The author has made a valuable contribution to instruction in biology. He has successfully avoided those abstruse statements with which physical chemists delight to bewilder biologists and yet has presented in adequate fashion the principles of physical chemistry most often used by students and research workers in the biological sciences. To them, particularly, this book is recommended.

D. B. DILL

**Photochemistry.** By D. W. G. STYLE, Ph.D. With a Preface by A. J. Allmand, M.C., D.Sc., F.R.S., Professor of Chemistry in the University of London, King's College. E. P. Dutton and Company, Inc., 286–302 Fourth Avenue, New York, 1931. vii + 96 pp. 9 figs. 11 × 17.5 cm. Price $1.10.

This excellent little book affords an approach to photochemistry "for the chemist who has not hitherto interested himself in the subject." There are five chapters, all entertainingly and clearly written. The large mass of factual material in the field is omitted and the author has chosen merely a few typical examples to be discussed in detail.

In the introductory Chapter a hasty survey is given of light absorption, reaction kinetics and line and band spectra. For the latter use is made of the Bohr atom and of the ideas of Franck, no mention being made of the newer forms of quantum mechanics. For the purposes of the book this omission is not serious, since the use of energy levels rather than their exact interpretation is of primary importance.

The Primary Light Process, Chain Reactions, the Dependence of the Quantum Yield on Temperature and Wave-length and Experimental Methods are taken up in the four succeeding chapters. The point of view is distinctly that of the chemist and not of the physicist and the author has, in some cases, discussed reaction mechanisms which are open to question. He has, however, been exceedingly candid in pointing out doubtful matters and the reader may feel assured that scientific accuracy has not been sacrificed to brevity.

The reviewer takes pleasure in recommending this book to those who may wish a brief survey of photochemistry as well as to many photochemists who may need to popularize their subject from time to time in conversation or in lecture. Indeed even the hardened addict is certain to find stimulating points of view on many topics.

W. ALBERT NOYES, JR.

**The Principles of Organic Chemistry.** By JAMES F. NORRIS, Professor of Organic Chemistry, Massachusetts Institute of Technology. Third edition. The McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1931. xii + 595 pp. 14.5 × 21 cm. Price, $3.00.

Though this volume ably maintains the Norris text in its proud position in the regard of organic chemists, enthusiasts for "electronics" will be disappointed by its conservative position. The new chapter on proteins strengthens the presentation of this important subject. The book is made unusually interesting by the accurate and specific information about industrial processes.

While actual reagents are, as a rule, indicated in the equations, there is still room for improvement in this matter: "O" or "H" not being very helpful to the inquiring student. Particularly where mechanisms of reactions are given, there is an opportunity for improvement in subsequent revisions of the text. In the discussion of the Perkin and the Beckmann reactions, and in the addition to $\alpha,\beta$-unsaturated acids this is apparent. The statement that ketones do not polymerize is included, and the stereoisomers of saccharic acid are said to be 16, whereas but 10 are possible. Also mention is made of disodium malonic ester though plenty of experimental evidence indicates that no such compound exists. It is unfortunate that one of the few errors of spelling involves the omission of the "h" in Winther's name.

However, these discrepancies, by contrast, but serve to emphasize the general excellence of this very teachable text.

G. ALBERT HILL

**Grenzflächenvorgänge in der unbelebten und belebten Natur. (Boundary Surface Reactions in Inanimate and Living Nature.)** By Prof. Dr. DAVID REICHINSTEIN. Verlag Johann Ambrosius Barth, Salomonstrasse 18B, Leipzig, Germany, 1930. xiv + 434 pp. 69 figs. 15.5 × 23.5 cm. Price, unbound, RM. 34.50; bound, RM. 36.50.

The content of this book covers such an immense field of science that the reviewer must content himself with making a report as to the fundamental idea jointly underlying the various chapters. This idea may be designated as the principle of substitution or replacement and may be characterized as follows.

When a reaction takes place at a phase boundary between a solid and a liquid such as adsorption, a rule may be stated as a substitute for what is known as the mass action law in a homogeneous system. The author takes the interfacial layer as a phase, this word being used as it is usually used in thermodynamics. Let the nature of the absorbing surface and the adjacent solvent be given and let a variable amount of another substance be dissolved in the solvent and partially adsorbed at the interface to the establishment of an equilibrium. In order to calculate the state of equilibrium by a principle resembling the mass action law the author propounds the following hypothesis.

The interfacial phase may be thought of as containing the molecules of the adsorbing solid and the molecules of the other substances concerned in a definite concentration. The sum of the concentrations of all these substances concerned must be taken as a constant so that by increasing the concentration of the substance to be adsorbed the concentration of the adsorbent is diminished. This idea, of course, cannot be taken literally because, from a molecular point of view, there is no sense in speaking of a concentration of the adsorbent in the interfacial phase. The whole idea is rather like an analogy.

A great part of the book is dedicated to the justification of the use of analogies in natural sciences and of the philosophy of "as though" especially with reference to Ernst Mach's philosophy. This principle is applied to processes of adsorption, catalysis, enzymes, immunology, medical problems, electrolysis, galvanic polarization, electron emission and others. The reviewer does not feel himself competent in all these various fields. In those fields in which he dares utter a criticism he feels that this principle solves the problem only in a formal way and disregards too much our well-established mental pictures about molecules and concentrations. To be sure, modern physics is inclined to abandon any mental picture or mechanistic

interpretation for intra-atomic processes such as electron orbits. But there was no need as yet to give up our mechanistic point of view when dealing with systems in which the molecule can be taken as the ultimate elementary mass unit. One is, however, on reading this remarkable book, so impressed by the display of the author's very comprehensive erudition and originality and by the strict treatment of the subject in other respects, that one feels judgment of the merits of the book may be left to the future. Albert Einstein accompanies this book with a preface. The following remark of his seems entirely to the point: "The hypothesis of a variable concentration of the solid participant of the reaction is very paradox from the standpoint of any molecular theory. Yet, however the decision finally may turn out, in any case this book may have an inspiring effect by its settings of the problems."

L. MICHAELIS

**Grundriss der modernen Arzneistoff-Synthese. (Fundamentals of Modern Medicinal Synthesis.)** By Dr. K. H. SLOTTA, Lecturer in Chemistry at the University of Breslau. Verlag von Ferdinand Enke, Stuttgart, Germany, 1931. xi + 202 pp. + 25 tables. 16 × 25 cm. Price, RM. 17.50, unbound; RM. 20, bound.

This outline of the synthesis of modern medicinals presents the subject from both chemical and pharmacological viewpoints.

The major classification of the material is pharmacological, the separate chapters being entitled: I, Narcotics; II, Sedatives and Hypnotics; III, Antipyretics; IV, Local Anesthetics; V, Sympathomimetics; VI, Excitants; and VII, Antiseptics and Chemotherapeutics. The subdivision of these major headings is generally along chemical lines. Thus, Chapter III is divided into A, Antipyrine Group, B, Phenacetine Group, C, Salicylic Acid Group and D, Atophan Group. Both author and subject indexes are provided. There are also, at the back of the book, 25 interesting and useful charts, depicting diagrammatically the synthesis of various important drugs and beginning with one on fundamental syntheses from carbon and lime, through acetylene. Structural formulas are used freely throughout the text, to make clear the various synthetic steps discussed and the constitution of the products. Type, paper and presswork are excellent.

The author has endeavored to show not only the details of the syntheses, but also to explain the pharmacological considerations underlying them. No attempt has been made to compile a work of such encyclopedic scope as Fränkel's "Die Arzneimittel-Synthese," but rather to select those medicinals of known constitution which have been introduced comparatively recently and have proved useful. The term "modern" is not interpreted as meaning only those synthetics to which a passing vogue or vigorous commercial exploitation may have given prominence, but includes such well-known compounds as ether and chloroform.

Since the book concerns medicinals in the broad sense, it takes up not only true curative agents, but also those compounds which stimulate or check the activity of various organs. Naturally, the chief aim of the synthesist is the preparation of healing drugs, but he must often content himself, at least temporarily, with those which merely cause the disappearance of the symptoms. General anesthetics are necessary for the performance of operations. In diseases of the nervous system, sleep is often one of the best healing agencies. Such indirect remedies as general anesthetics, hypnotics, etc., therefore are included. Other maladies may be alleviated by the introduction of synthetics which the body itself either ceases to generate or no longer produces in sufficient amount, as, for example, adrenaline or thyroxine.

The chapter on "antiseptics and chemotherapeutics" is devoted to a consideration of those synthetics which act either to destroy pathogenic organisms or at least to arrest their growth, and which are therefore true remedies in that they remove the cause of the disease.

The book is as nearly up to date as reasonably can be expected. The subject matter is presented clearly and compactly, with ample references to the original literature, and the reviewer is of opinion that the work will be found useful to all interested in this exceedingly important branch of Organic Chemistry.

Of course, no two chemists would agree exactly on the list of synthetics which should be presented in such an outline, and it is inevitable that there will be those who will criticize it on that score, but it seems to the reviewer that on the whole the list has been chosen wisely and with reasonable conservatism, and that the author has kept constantly in mind that the guiding star in all such investigations is the desirability of learning more about the connection between chemical constitution and physiological action.

MARSTON TAYLOR BOGERT

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## BOOKS RECEIVED

November 15, 1931–December 15, 1931

GUIDO BARGELLINI. "Esercizi Numerici di Chimica Organica." Editrice Studium, Piazza S. Agostino 20-a, Roma, Italy. 242 pp.

GEORGE BARGER. "Ergot and Ergotism." A Monograph Based on the Dohme Lectures Delivered in Johns Hopkins University, Baltimore. Gurney and Jackson, 33 Paternoster Row, E. C., London, England. 279 pp. 15s net.

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## THE EFFECT OF THE SOLVENT UPON THE ACTIVITY OF ACIDS: THE VAPOR PRESSURE OF HYDROGEN CHLORIDE IN GLACIAL ACETIC ACID SOLUTIONS


BY WORTH H. RODEBUSH AND ROSWELL H. EWART



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The idea that the basicity of the solvent is an important factor in the ionization of acids has been discussed by many authors. Latimer and Rodebush[1] have given a discussion of the interaction of the attractive forces between solvent and hydrogen ion, by which the dissociation is largely determined.

More recently Conant, Hall and others have studied the behavior of acids in non-aqueous solvents by means of electromotive force measurements. Since the results of these measurements indicate a high degree of activity for the hydrogen ion, the term "superacid" has been employed to characterize the usual behavior of non-aqueous solutions of acid.

This term is something of a misnomer from the thermodynamic standpoint, since as has been pointed out by Taylor, Guggenheim[2] and others we do not measure individual ion activities, but rather the mean activity of a pair of ions. A further complication is the fact that the activity of the ions in the non-aqueous solvent is referred to the standard state of the water solution.[3]

Nevertheless the term has a certain justification since the behavior of the acid in solution probably depends chiefly on the coördination of solvent molecules by the hydrogen ion. The coördination number of the hydrogen ion is presumably two. In a basic solvent with high dielectric constant, the acid appears to be highly ionized. If the dielectric constant is low the

[1] For earlier references see (a) Abegg and Bodländer, *Z. anorg. Chem.*, **20**, 453 (1899); (b) Kraus and Bray, THIS JOURNAL, **35**, 1337 (1913); (c) Latimer and Rodebush, *ibid.*, **42**, 1419 (1920). The principal references to the recent literature are summarized in the following papers: (d) Conant and Hall, *ibid.*, **49**, 1412 (1927); (e) Hammett, *ibid.*, **50**, 2666 (1928); (f) La Mer and Downes, *ibid.*, **53**, 888 (1931); (g) Wynne Jones, *J. Chem. Soc.*, 1065 (1930).

[2] Taylor, *J. Phys. Chem.*, **31**, 1478 (1927); Guggenheim, *ibid.*, **33**, 842 (1929).

[3] For a discussion of the difficulties involved here see Guggenheim, *ibid.*, **34**, 1540 (1930).

reaction between solvent and acid takes place just the same, but a hydrogen bond is now formed and the acid is not ionized.[1c] In the same way an acid may react with an indicator without ionization. The activity of an acid in solution therefore would seem to depend mainly upon the coördination of the solvent by the hydrogen ion and to a much less degree upon any physical property of the solvent as dielectric constant, especially as in most non-aqueous solvents the degree of ionization is small.

Hall and Werner[4] have pointed out that solutions of hydrogen chloride in acetic acid are not suitable for electromotive force measurements. By the same token such solutions are suitable for vapor pressure measurements and the escaping tendency of the hydrogen chloride is measured directly. A $P_H$ measurement can only give the same thing with the attendant uncertainties of liquid junction potential.

It is not difficult to predict the behavior of an acid. Suppose we have hydrogen chloride vapor at a partial pressure of 100 mm. in equilibrium with various solvents. The escaping tendency of the hydrogen chloride must be the same in all solvents. In water a very large amount of hydrogen chloride is dissolved, while in a solvent such as benzene, which cannot be coördinated by the hydrogen ion at all, the amount of hydrogen chloride is at most that predicted for an ideal solution. The disparity between activity and concentration must therefore be very great provided the activities in both solutions are referred to a common standard state. Or put in another way the escaping tendency of hydrogen chloride is very low from a 1.0 molal water solution and very high from a 1.0 molal benzene solution. The same result must be obtained by any measurement of activity, for example, in reactions with indicators, regardless of whether water must be present to catalyze the reaction or not, since the activity is that of the vapor above the solution.

The behavior of an acid like perchloric is of course similar to that of hydrogen chloride. It is not volatile and hence, provided it is miscible with a solvent, solutions of very high activity may be prepared. On the other hand, since the normal state of a weak acid molecule in water is the unionized form and since this molecule may form a more nearly ideal solution with non-aqueous solvents than with water there is no reason why the activity of weak acids should appear to be increased in non-aqueous solvents.

In a solvent such as benzene which is not basic and which has a low dielectric constant, the ionization and the electrical conductivity must be very small indeed. The change of conductivity with concentration in solutions of low dielectric constant was explained by Latimer and Rodebush;[1c] the explanation given by Gross and Halpern[5] comes to the same thing although expressed in a different terminology.

[4] Hall and Werner, THIS JOURNAL, **50**, 2367 (1928).

[5] Gross and Halpern, *Physik. Z.*, **26**, 636 (1925).

## Experimental

**General Method.**—The vapor pressure of hydrogen chloride from glacial acetic acid solutions was determined by a dynamic method. A known volume of dry air was drawn through the saturating tubes which were filled with the solution. The air then passed through an absorption tube which removed the hydrogen chloride and acetic acid vapors. The quantities of hydrogen chloride and acetic acid vaporized were determined by analysis.

**Description of Apparatus.**—The general set-up of apparatus was similar to that of Pearce and Snow[6] except that the volume of air which passed through the saturators was determined by displacement of water, correction being made for temperature, total pressure and partial pressure of the water vapor of the measured volume of air. The saturators were of the type used by Bichowsky and Storch.[7] The absorption tube was of the same form as the saturator tubes. In order to prevent condensation on the walls of the connecting tubes, the absorption tube filled with standardized sodium hydroxide solution, as well as the saturators, was kept immersed in a thermostat held at 24.85 ± 0.02°.

## Materials

**Glacial Acetic Acid.**—Three liters of Grasselli "Strictly C. P. Acid (99.5%)" was distilled from a five-liter flask over chromic oxide. The first and last 300 cc. were rejected. The middle portion was frozen slowly with almost constant agitation. The unfrozen center liquor was drained off. The frozen acid was then allowed to melt and was stored in sealed bottles. This now analyzed 99.7% acetic acid.

**Saturation with Hydrochloric Acid.**—Three hundred cc. of the pure acetic acid was partly saturated with dry hydrochloric acid gas. The hydrogen chloride was prepared by the action of C. P. 95% sulfuric acid on C. P. sodium chloride, and passed through a column containing glass wool to remove any sulfuric acid mist. This hydrogen chloride–acetic acid mixture was then diluted with the pure acetic acid as required. Previously, using the unpurified glacial acetic, the hydrogen chloride–acetic acid mixtures had a pale straw color. The mixtures using the purified acid were quite colorless.

**Standard Solutions.**—The standard acid was made up and its normality determined in the usual manner against standard sodium carbonate. The half normal sodium hydroxide which was used in the absorption tube was titrated against this acid. Chlorides were run gravimetrically and volumetrically by the Mohr and the Volhard methods. The Volhard method gave the best results and was used in all the final runs.

**Manipulation.**—The apparatus was sealed together and the saturators filled with about 140 cc. of the hydrochloric–acetic acid mixture. While this was being done a gentle stream of air was passed through the absorption tube to prevent acid vapors from collecting in this tube. The air stream was then turned off and 30.00 cc. of half normal sodium hydroxide was added from a buret to the absorption tube and then water was added until the top of the inner bubbler tube was just covered. These tubes were then sealed and the whole apparatus which was held in a frame was lowered into the thermostat and sealed to the displacement bottle. It was necessary to have a small constriction in the line from this bottle to the absorption tube in order to prevent irregularities in flow which would otherwise cause the air to by-pass through the holes in the bottom of the bubbler tubes and thus it might not become completely saturated.

The measurement of the displaced air was started when the first bubble appeared

[6] Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

[7] Bichowsky and Storch, THIS JOURNAL, **37**, 2696 (1915).

in the absorption tube. When one liter of the water, which had been previously saturated with air, had been displaced the flow was shut off. The manometer on the displacement bottle was read as soon as equilibrium was reached. The temperature of the water in this bottle was taken and the contents of the absorption tube analyzed. The hydrochloric–acetic acid mixtures were analyzed before and after each run. The variation was usually less than 3% and by using the average analysis very little error is introduced.

The vapor pressures were calculated using the equation

$$P = \frac{(P_1 - P_3)}{(P_2V_2/mRT_2 + 1)}$$

TABLE I

ANALYTICAL DATA AND CALCULATED VAPOR PRESSURES OF HYDROCHLORIC ACID

| Run | $P_1$, pressure in mm. | $V_2$, liters (vol. of air = vol. of water) | Partial press. of air | $T_2$, air temp. °K. | $m$, HCl, mole of HCl in absorption tube | $m$, AcOH mole of AcOH in absorption tube | $C$, av. % HCl in glacial AcOH | $N_2$ mole fraction of HCl in glacial AcOH | $P$, partial vapor press. of HCl, mm. |
|---|---|---|---|---|---|---|---|---|---|
| 24 | 746.0 | 1.000 | 722.2 | 296.8 | 0.005700 | 0.001619 | 1.270 | 0.0208 | 93.0 |
| 25 | 745.6 | 1.000 | 720.9 | 297.4 | .003406 | .001559 | 0.836 | .0137 | 58.8 |
| 15 | 739.6 | 1.000 | 718.4 | 294.5 | .003079 | .001589 | .70 | .0115 | 52.8 |
| 16 | 742.9 | 1.000 | 718.8 | 297.2 | .002920 | .001698 | .67 | .0110 | 50.9 |
| 17 | 749.6 | 1.000 | 724.9 | 297.2 | .002669 | .001667 | .640 | .0105 | 46.9 |
| 18 | 744.8 | 1.051 | 721.2 | 297.4 | .001852 | .001680 | .423 | .00695 | 31.6 |
| 19 | 743.7 | 1.000 | 715.8 | 298.6 | .001570 | .001643 | .385 | .00632 | 28.6 |
| 20 | 747.5 | 1.000 | 723.9 | 296.7 | .000946 | .001616 | .247 | .00406 | 17.3 |
| 21 | 746.7 | 1.000 | 717.5 | 299.8 | .000806 | .001588 | .212 | .00349 | 15.0 |
| 22 | 741.7 | 1.013 | 715.9 | 297.6 | .000514 | .001725 | .125 | .00206 | 9.4 |
| 23 | 744.1 | 1.000 | 718.3 | 297.5 | .000524 | .001690 | .147 | .00242 | 9.7 |

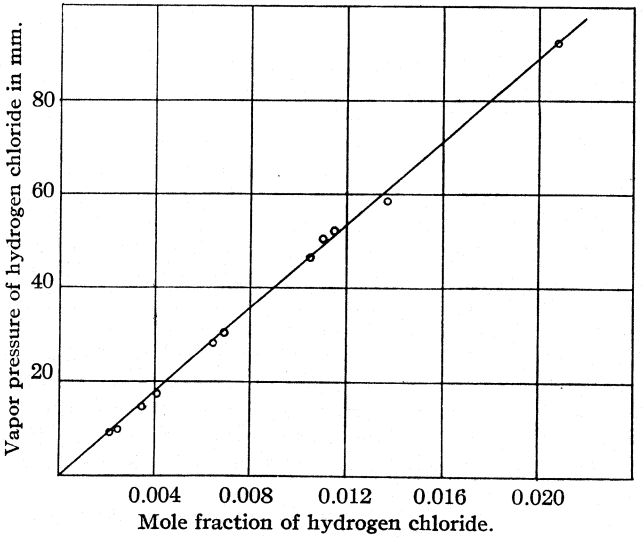


Fig. 1.—Vapor pressure of hydrogen chloride from glacial acetic acid solutions at 24.8°.

where $P_3$ is the vapor pressure of acetic acid or 15.6 mm.[8] at 25°, and $m$ is the number of moles of hydrochloric acid in the absorption tube. The other symbols are as given in Table I.

**Results.**—The vapor pressure curve over the range studied is a straight line function of the mole fraction. It may be seen that since the partial vapor pressure of the hydrogen chloride from a glacial acetic acid solution for which the mole fraction of hydrogen chloride is 0.011 is 50.9 mm. and since the corresponding partial vapor pressure from an aqueous solution of the same mole fraction is only about 0.0001 mm.,[9] the relative activity is more than a hundred thousand times greater in the former case. Earlier results on much stronger solutions indicate a sharp increase in the slope of the curve. The following approximate results are given: 5% hydrochloric acid, 470 mm.; 3% hydrochloric acid, 300 mm.

## Summary

A discussion is given of the effect of solvent upon the activity of acids in solution together with measurements of the vapor pressure of hydrogen chloride in glacial acetic solution.

[8] "International Critical Tables."

[9] *Ibid.*, Vol. 3.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

# THE THERMODYNAMIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS FROM 0 TO 40°

BY HERBERT S. HARNED AND LESLIE F. NIMS[1]

RECEIVED JULY 17, 1931 PUBLISHED FEBRUARY 5, 1932

Although flowing amalgam cell measurements have been used with considerable success to determine the activity coefficients of alkali and alkaline earth halides at 25°, few reliable measurements are available at other temperatures. The present communication contains electromotive force measurements of the cells

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{NaCl}\ (m_2) \mid \mathrm{Na}_x\mathrm{Hg} \mid \mathrm{NaCl}\ (0.1) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

from which the activity coefficient and partial molal heat content of sodium chloride have been computed through a concentration range from 0 to 4 $M$ and a temperature range of from 0 to 40° at 5° intervals.

## Experimental Procedure and Results

All precautions pertaining to accurate flowing amalgam cell measurements were taken.[2] A vacuum technique was employed which excluded

[1] This paper contains the material and calculations originally presented by Leslie F. Nims to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

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

dissolved air from the solutions which came in contact with either the amalgam or the silver–silver chloride electrodes. Carefully repurified salt was used. The silver chloride electrodes were of the kind designated by Harned as Type 2, and were prepared from very carefully purified silver oxide paste by electrolysis. A new silver–silver chloride electrode was made for each measurement. The sodium amalgam of 0.02% sodium was made according to the customary method.[3] A small correction was added to the electromotive forces to compensate for the slight changes in concentrations of the solutions caused by the boiling in vacuo which was employed to remove the dissolved air. Consequently, all the results are reported at round concentrations. Since measurements were at eight temperatures, the thermostat was equipped with eight thermoregulators set for the desired temperatures. This facilitated operations considerably.

Table I contains the observed electromotive forces which represent the mean of the number of separate cell measurements given in the column immediately preceding. It is important to note that every measurement was made with a freshly constructed cell, since with cells of this type it is not practicable to measure the same cell at a series of temperatures.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

Ag | AgCl | NaCl ($m$) | $Na_xHg$ | NaCl (0.1) | AgCl | Ag

| $m$ | No. of cells | $E$ 0.3°C. | No. of cells | $E$ 12.5°C. | No. of cells | $E$ 15°C. | No. of cells | $E$ 20°C. |
|---|---|---|---|---|---|---|---|---|
| 0.05 | 4 | −0.02970 | | | 4 | −0.03151 | 5 | −0.03209 |
| 0.2 | 4 | .02964 | 2 | 0.03102 | 6 | .03137 | 6 | .03214 |
| 0.5 | 4 | .06876 | 2 | .07254 | 4 | .07304 | 8 | .07425 |
| 1.0 | 6 | .09876 | 2 | .10437 | 4 | .10562 | 5 | .10741 |
| 1.5 | 2 | .11726 | | | 2 | .12533 | 6 | .12784 |
| 2.0 | 2 | .13099 | 2 | .13898 | 2 | .14044 | 2 | .14339 |
| 2.5 | 6 | .14267 | | | 4 | .15286 | 2 | .15625 |
| 3.0 | 2 | .15261 | 2 | .16196 | 4 | .16390 | 2 | .16751 |
| 3.5 | 2 | .16162 | | | 4 | .17351 | 2 | .17738 |
| 4.0 | 2 | .16996 | 2 | .18074 | 3 | .18282 | 2 | .18655 |

| $m$ | No. of cells | $E$ 25°C. | No. of cells | $E$ 30°C. | No. of cells | $E$ 37.5°C. | No. of cells | $E$ 40°C. |
|---|---|---|---|---|---|---|---|---|
| 0.05 | 4 | −0.03245 | 2 | −0.03290 | 2 | −0.03377 | 2 | −0.03401 |
| 0.2 | 4 | .03252 | 2 | .03314 | 2 | .03357 | 2 | .03414 |
| 0.5 | 2 | .07584 | 2 | .07686 | 2 | .07875 | 2 | .07954 |
| 1.0 | 6 | .10955 | 4 | .11128 | 4 | .11417 | 6 | .11529 |
| 1.5 | 2 | .13041 | 4 | .13249 | 4 | .13618 | 5 | .13740 |
| 2.0 | 2 | .14627 | 4 | .14892 | 4 | .15279 | 2 | .15427 |
| 2.5 | 8 | .15925 | 4 | .16213 | 2 | .16648 | 4 | .16804 |
| 3.0 | 4 | .17070 | 2 | .17396 | 2 | .17855 | 3 | .18031 |
| 3.5 | 4 | .18094 | 4 | .18422 | 2 | .18916 | 2 | .19091 |
| 4.0 | 5 | .19036 | 2 | .19380 | 2 | .19920 | 2 | .20100 |

[3] Harned, THIS JOURNAL, **47**, 677 (1925).

**A Graphical Method of Determination of the Temperature Coefficient.**—The equation for the cells of the type under consideration may be written

$$E - \frac{2RT}{F} \ln \frac{m}{0.1} = \frac{2RT}{F} \ln \frac{\gamma}{\gamma_{0.1}} \qquad (1)$$

If the left side of this equation be plotted against the temperature, a very sensitive series of graphs is obtained from which the electromotive forces at 5° temperature intervals may be read with a very high degree of accuracy.

If the first order differences of the electromotive forces at equal temperature intervals of cells of constant composition of this type and of other types containing uni-univalent electrolytes be plotted against the temperature, the plots are straight lines. That this relation is valid from 0 to 40° to within ±0.01 to 0.02 millivolt is shown by Fig. 1, in which the values of

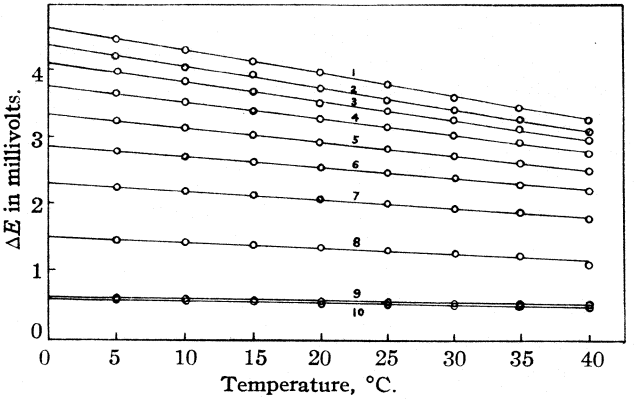


Fig. 1.—Variation of the first order difference of electromotive force with temperature: (1) 4 *M* (2) 3.5 *M* (3) 3 *M* (4) 2.5 *M* (5) 2 *M* (6) 1.5 *M* (7) 1 *M* (8) 0.5 *M* (9) 0.2 *M* (10) 0.05 *M*.

$\Delta E$, the first order differences of the electromotive forces, are plotted against the temperature. This fact shows that for the case under consideration, the usual equation for computing temperature coefficients

$$E_T = E_{T_0} + a_{T_0}(T - T_0) + b(T - T_0)^2 \qquad (2)$$

is sufficient to express exactly the experimental results without the introduction of a third term of the power series.

To obtain the constants of this equation, the following method was adopted. Let $T_0$ be a reference temperature. For a series of electromotive forces at intervals of temperature of 5°, the equations

$$\left.\begin{aligned}
E_{T_0+15} &= \ldots\ldots \\
E_{T_0+10} &= E_{T_0} + a_{T_0} \cdot 10 + b \cdot 10^2 \\
E_{T_0+5} &= E_{T_0} + a_{T_0} \cdot 5 + b \cdot 5^2 \\
E_{T_0} &= E_{T_0} \\
E_{T_0 \rightarrow 5} &= E_{T_0} - a_{T_0} \cdot 5 + b \cdot 5^2 \\
E_{T_0-10} &= E_{T_0} \rightarrow a_{T_0} \cdot 10 + b \cdot 10^2 \\
E_{T_0-15} &= \ldots\ldots
\end{aligned}\right\} \qquad (3)$$

are easily obtained from equation (2). The first order differences are then seen to be given by

$$\left.\begin{aligned} E_{T_0+15} &= \ldots\ldots \\ E_{T_0+10} &= 5\,a_{T_0} + 75\,b \\ E_{T_0+5} &= 5\,a_{T_0} + 25\,b \\ E_{T_0} &= 5\,a_{T_0} - 25\,b \\ E_{T_0-5} &= 5\,a_{T_0} - 75\,b \\ E_{T_0-10} &= \ldots\ldots \end{aligned}\right\} \quad (4)$$

and the general equation for the first order differences is

$$\Delta E_T = 5\,a_{T_0} - b\,[25 + (T_0 - T)10] \quad (5)$$

This is the equation for the family of straight lines in Fig. 1. Upon differentiation

$$\frac{\partial \Delta E_T}{\partial T} = 10\,b \quad (6)$$

so that $b$ is 0.1 of the slope of the plots in Fig. 1, a condition which makes the numerical evaluation of $b$ very accurate. $b$ is independent of the reference temperature.

When $T$ equals $T_0$

$$\Delta E_T = \Delta E_{T_0} = 5\,a_{T_0} - 25\,b \quad (7)$$

and equals the ordinate readings at this temperature. From this

$$a_{T_0} = \frac{\Delta E_{T_0}}{5} + 5\,b \quad (7a)$$

an equation by which $a_{T_0}$ may readily be computed, and which shows that $a_{T_0}$ depends on the temperature chosen as reference. Further, upon differentiation of equation (2), we obtain

$$\frac{\partial E}{\partial T} = a_{T_0} + 2\,b\,(T - T_0) \quad (8)$$

which becomes

$$\left.\frac{\partial E}{\partial T}\right]_{T=T_0} = a_{T_0} = \frac{\Delta E_{T_0}}{5} + 5\,b \quad (9)$$

when $T = T_0$. Since $b$ is small, the temperature coefficient at $T = T_0$ approaches $\Delta E_{T_0}/5$.

From equation (9) it is seen that the accuracy with which $\partial E/\partial T$ may be obtained depends upon the accuracy of evaluation of $\Delta E$. Little difficulty was encountered except with the results at salt concentrations above 2.5 $M$. This is caused by an uncertainty introduced by the appreciable solubility of the silver chloride in the concentrated salt solutions, which causes an indeterminate error of the order of a few tenths of a millivolt. This difficulty was overcome to a certain extent by plotting $\Delta E$ against the log $m$ at constant temperature. By combining these plots with those at constant composition given in Fig. 1, the above uncertainty was partially removed. In any case, the accuracy in the determination of $\partial E/\partial T$ is thought to be 1% in all cases, and better than 1% in the more favorable cases at the lower concentrations.

Table II contains the electromotive forces at 5° intervals determined by this graphical method, as well as the values of $a$ and $b$ of equation (2).

TABLE II

(1) ELECTROMOTIVE FORCES OF THE CELLS: Ag | AgCl | NaCl ($m$) | $Na_xHg$ | NaCl (0.1) | AgCl | Ag, FROM 0 TO 40° AT 5° INTERVALS

| $T$, °C. | $m$ = 0.05 | $m$ = 0.2 | $m$ = 0.5 | $m$ = 1.0 | $m$ = 1.5 |
|---|---|---|---|---|---|
| 0 | 0.02966 | 0.02957 | 0.06867 | 0.09882 | 0.11708 |
| 5 | .03126 | .03019 | .07015 | .10109 | .11990 |
| 10 | .03084 | .03079 | .07160 | .10330 | .12263 |
| 15 | .03141 | .03138 | .07301 | .10545 | .12528 |
| 20 | .03196 | .03195 | .07438 | .10753 | .12784 |
| 25 | .03250 | .03251 | .07571 | .10955 | .13032 |
| 30 | .03302 | .03305 | .07700 | .11151 | .13272 |
| 35 | .03353 | .03358 | .07825 | .11341 | .13503 |
| 40 | .03402 | .03409 | .07946 | .11524 | .13725 |
| 25[4] | | .03247 | .07566 | .10957 | .13033 |

| | $m$ = 2.0 | $m$ = 2.5 | $m$ = 3.0 | $m$ = 3.5 | $m$ = 4.0 |
|---|---|---|---|---|---|
| 0 | 0.13096 | 0.14214 | 0.15215 | 0.16136 | 0.16969 |
| 5 | .13422 | .14581 | .15615 | .16559 | .17418 |
| 10 | .13738 | .14936 | .16000 | .16965 | .17850 |
| 15 | .14043 | .15278 | .16370 | .17356 | .18265 |
| 20 | .14338 | .15607 | .16727 | .17731 | .18663 |
| 25 | .14622 | .15923 | .17070 | .18090 | .19044 |
| 30 | .14896 | .16227 | .17398 | .19433 | .19407 |
| 35 | .15159 | .16518 | .17711 | .18760 | .19755 |
| 40 | .15412 | .16796 | .18010 | .19071 | .20085 |
| 25[4] | .14621 | .15923 | .17037 | .18088 | .19079 |

(2) CONSTANTS OF EQUATION (2) $E_T = E_{T_0} + a_{T_0}(T-T_0) + b(T-T_0)^2$; $T_0 = 298.1$

| $m$ | 0.05 | 0.2 | 0.5 | 1.0 | 1.5 |
|---|---|---|---|---|---|
| $a \times 10^{-6}$ | 106 | 110 | 262 | 398 | 487 |
| $b \times 10^{-6}$ | −0.30 | −0.30 | −0.78 | −1.24 | −1.68 |
| $m$ | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 |
| $a \times 10^{-6}$ | 558 | 620 | 670 | 702 | 745 |
| $b \times 10^{-6}$ | −2.10 | −2.54 | −2.88 | −3.18 | −3.40 |

**The Partial Molal Heat Content of Sodium Chloride.**—The partial molal heat content referred to the 0.1 $M$ reference solution may readily be computed from the above electromotive forces. By substituting the value for the temperature coefficient of electromotive force given by equation (9) in the Gibbs–Helmholtz equation

$$(-\Delta\bar{H}) = NF\left[E - T\left(\frac{\Delta E_{T_0}}{5} + 5b\right)\right] \qquad (10)$$

[4] In this row are the results obtained by Harned [THIS JOURNAL, **51**, 416 (1929)] at 25°. Up to 2.5 $M$ the agreement between the two series of observations is excellent since the differences are considerably less than 0.05 millivolt in five out of the six observations. At 3 $M$ and 4 $M$, the agreement is not nearly so good, a fact which we attribute to the solubility of the silver chloride.

is readily obtained. By means of this equation, the partial heat content changes corresponding to the transfer NaCl ($m$) to NaCl (0.1) were obtained. These are given in Table III, and their graphs are in Fig. 2.

TABLE III

THE PARTIAL MOLAL HEAT OF DILUTION OF SODIUM CHLORIDE SOLUTIONS REFERRED TO THE 0.1 $M$ SOLUTION

| $m$ | $\sqrt{m}$ | 0° | 5° | 10° | 15° | 20° | 25° | 30° | 35° | 40° |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.05 | 0.224 | 81 | 62 | 44 | 23 | 2 | − 16 | − 37 | − 60 | −81 |
| .1 | .316 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| .2 | .447 | − 108 | − 90 | − 69 | − 51 | − 30 | − 9 | 12 | 32 | 53 |
| .5 | .707 | − 309 | − 258 | − 209 | − 157 | −103 | − 76 | − 2 | 58 | 115 |
| 1.0 | 1.000 | − 630 | − 549 | − 468 | − 383 | −302 | −214 | −129 | − 39 | 55 |
| 1.5 | 1.224 | − 907 | − 800 | − 688 | − 572 | −459 | −341 | −221 | −101 | −23 |
| 2.0 | 1.414 | −1150 | −1020 | − 884 | − 748 | −607 | −466 | −321 | −173 | −28 |
| 2.5 | 1.581 | −1425 | −1265 | −1097 | − 932 | −761 | −588 | −411 | −232 | −51 |
| 3.0 | 1.732 | −1615 | −1435 | −1250 | −1065 | −872 | −678 | −466 | −265 | −60 |
| 3.5 | 1.871 | −1710 | −1505 | −1300 | −1085 | −872 | −656 | −434 | −208 | 23 |
| 4.0 | 2.000 | −1850 | −1633 | −1415 | −1190 | −962 | −732 | −480 | −267 | −12 |

The dashed line in the figure represents the results obtained by Lewis and Randall at 25°.[5] The form of the curve is the same, but the numerical

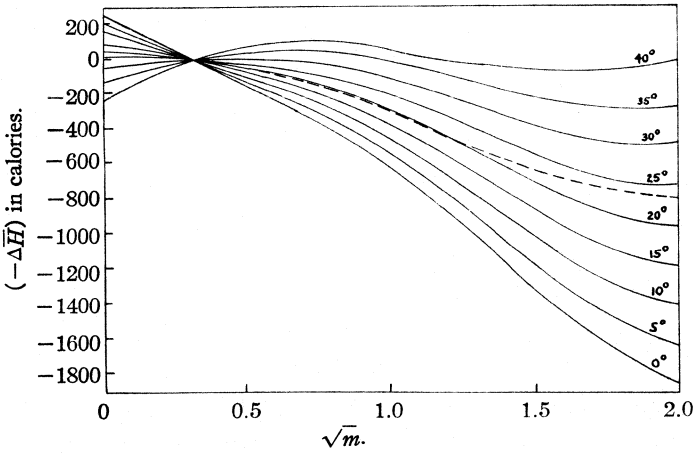


Fig. 2.—Partial molal heat of dilution of sodium chloride in aqueous solution referred to the 0.1 $M$ solution.

agreement is approximate. A part of this discrepancy is due to the fact that the values obtained by Lewis and Randall were computed from calorimetric data by a method which involved extrapolation to infinite dilution and the use of estimated partial specific heats.

Further, it should be mentioned that plots of these partial heats of dilu-

[5] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, Chapter VIII, Table 5.

tion against the temperature give a family of straight lines. Since the partial specific heats are known to be practically independent of the temperature, the straight line relation is to be expected because the slopes equal the differences in partial molal specific heats of the solutions at concentrations $m$ and the partial molal specific heat of the 0.1 $M$ solution. The partial molal specific heat of sodium chloride in aqueous solution at 25° has recently been redetermined from calorimetric data by Randall and Rossini.[6] In Table IV we have compared their results with the values computed from $\overline{C}_p - \overline{C}_{p_{0.1}}$ which were determined from the slopes of the plots of $(-\Delta H)$ against $T$. The values of $\overline{C}_p - \overline{C}_{p_{0.1}}$ thus obtained were plotted against $m^{1/2}$ and were found to lie on a straight line with a slope of 24.8. By taking $\overline{C}_{p_0}$ at zero salt molality equal to −23.3 cal., as found by Randall and Rossini, the results in the third column of the table were compiled from this plot.

TABLE IV

COMPARISON OF THE PARTIAL MOLAL HEAT CAPACITIES WITH RESULTS OBTAINED FROM CALORIMETRIC MEASUREMENTS

| $m$ | $\overline{C}_p$ (R. and R.), cal. | $\overline{C}_p$ (H. and N.), cal. |
|---|---|---|
| 0.00 | −23.3 | (−23.3) |
| .05 | −18.9 | −17.7 |
| .1 | −17.0 | −15.5 |
| .2 | −14.2 | −12.2 |
| .5 | − 8.6 | − 5.7 |
| 1 | − 2.3 | + 1.5 |
| 1.5 | + 2.6 | + 7.1 |
| 2 | + 6.9 | +11.8 |
| 2.5 | +10.65 | +15.9 |

The values determined from electromotive force measurements may be represented by $\overline{C}_p = 24.8\ m^{1/2} - 23.3$, those determined by Randall and Rossini by $\overline{C}_p = 21\ m^{1/2} - 23.3$. Thus, the slopes determined by the two methods differ somewhat from each other, but, considering the difficulties pertaining to both methods and the smallness of the heat magnitudes involved, we consider the agreement fairly satisfactory. The advantage of the present method of determining the slope lies in its simplicity and in the fact that straight line functions were used in deriving the values.

**The Activity Coefficients of Sodium Chloride Solutions from 0 to 40°.**— The activity coefficients of sodium chloride may be calculated from the electromotive force data by Hückel's equation[7]

$$\log \gamma = -\frac{u\sqrt{c}}{1 + A\sqrt{2c}} + B \cdot 2c - \log (1 + 0.036m) \qquad (11)$$

The constants $A$ and $B$ have been evaluated at 0, 25 and 40° and are given in Table V, section (1). Harned[4] obtained 0.84 and 0.032 for $A$

[6] Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

[7] Hückel, *Physik. Z.*, **26**, 83 (1925).

and $B$ at 25°. Section (2) of the table gives the comparison between the observed results computed directly by equation (1) and those calculated by equation (11) at these temperatures. Section (3) gives the experimentally determined values at the 5° temperature intervals from 0 to 40°, and a concentration range of from 0.05 to 4 $M$.

TABLE V

ACTIVITY COEFFICIENTS

(1) Values of Constants of Equation 11

| | 0° | 25° | 40° |
|---|---|---|---|
| $D$..... | 88.06 | 78.51 | 73.36 |
| $u$..... | 0.4864 | 0.5067 | 0.5212 |
| $A$..... | .740 | .837 | .887 |
| $B$..... | .0264 | .0316 | .0323 |

(2) Comparison of Observed Activity Coefficients with Those Computed by Equation 11 at 0, 25 and 40°

| | 0° | | 25° | | 40° | |
|---|---|---|---|---|---|---|
| $m$ | $\gamma_{calcd.}$ | $\gamma_{ex.}$ | $\gamma_{calcd.}$ | $\gamma_{ex.}$ | $\gamma_{calcd.}$ | $\gamma_{ex.}$ |
| 0.05 | 0.820 | 0.823 | 0.818 | 0.820 | 0.816 | 0.819 |
| .1 | ( .773) | ( .773) | ( .773) | ( .773) | ( .771) | ( .771) |
| .2 | .724 | .724 | .727 | .727 | .726 | .725 |
| .5 | .662 | .664 | .675 | .675 | .675 | .673 |
| 1.0 | ( .631) | ( .631) | ( .654) | ( .652) | ( .657) | ( .653) |
| 1.5 | .623 | .620 | .657 | .651 | .662 | .654 |
| 2.0 | .626 | .624 | .669 | .665 | .676 | .671 |
| 2.5 | ( .634) | ( .634) | ( .686) | ( .686) | ( .693) | ( .693) |
| 3.0 | .645 | .653 | .694 | .714 | .717 | .723 |
| 3.5 | .651 | .680 | .723 | .747 | .734 | .758 |
| 4.0 | .660 | .710 | .754 | .786 | .767 | .797 |

(3) Experimental Activity Coefficients

| $m$ | 0° | 5° | 10° | 15° | 20° | 25° | 30° | 35° | 40° |
|---|---|---|---|---|---|---|---|---|---|
| 0.05 | 0.823 | 0.822 | 0.822 | 0.821 | 0.821 | 0.820 | 0.822 | 0.822 | 0.819 |
| .1 | .773 | .773 | .773 | .773 | .773 | .773 | .773 | .773 | .771 |
| .2 | .724 | .726 | .727 | .727 | .727 | .727 | .727 | .727 | .725 |
| .5 | .664 | .669 | .670 | .672 | .674 | .675 | .675 | .675 | .673 |
| 1.0 | .631 | .637 | .642 | .646 | 649 | .652 | .653 | .654 | .654 |
| 1.5 | .620 | .629 | .636 | .642 | .647 | .651 | .654 | .655 | .654 |
| 2.0 | .624 | .636 | .645 | .653 | .660 | .665 | .670 | .671 | .671 |
| 2.5 | .634 | .652 | .660 | .671 | .679 | .686 | .691 | .694 | .693 |
| 3.0 | .653 | .670 | .684 | .696 | .706 | .714 | .720 | .723 | .723 |
| 3.5 | .680 | .699 | .714 | .728 | .738 | .747 | .752 | .755 | .758 |
| 4.0 | .710 | .732 | .749 | .765 | .777 | .786 | .793 | .797 | .797 |

Figure 3 contains a plot of the activity coefficients against $\sqrt{m}$ at all the temperatures at which it was studied. It is interesting to note that, as the temperature increases, there is a diminishing difference between the values at 5° intervals. Thus, if at a given concentration, $\gamma$ be plotted against the temperature, it is found that $\gamma$ approaches a maximum value. Indeed,

there is evidence from other sources that this is a true maximum and that above a certain temperature $\gamma$ will decrease.

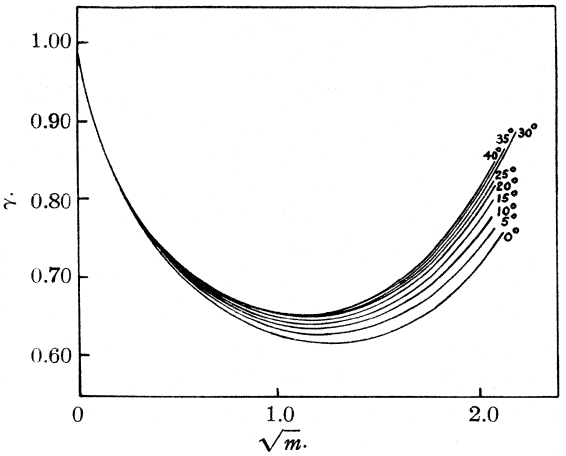


Fig. 3.—Experimental activity coefficients.

In Fig. 4 both the $A$ and $B$ constants of Hückel's equation are plotted against the temperature. Both increase with $T$. $A$ varies approximately linearly, whereas $B$ approaches a maximum value.

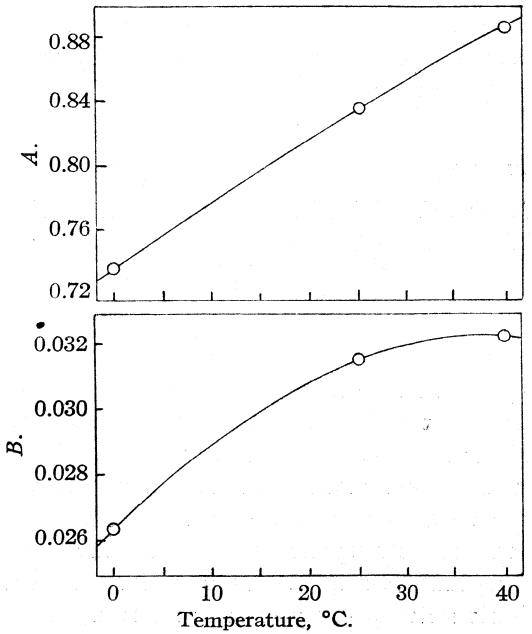


Fig. 4.—The $A$ and $B$ constants of the Hückel equation as a function of the temperature.

## Summary

1. Accurate electromotive force measurements of the cells

$$Ag \mid AgCl \mid NaCl\ (m) \mid Na_xHg \mid NaCl\ (0.1) \mid AgCl \mid Ag$$

have been made at 0, 12.5, 15, 20, 25, 30, 37.5 and 40°.

2. The first order difference of the electromotive force varies linearly with the temperature. This fact helps considerably in obtaining the electromotive forces at 5° temperature intervals and affords a very accurate method of obtaining the constants of the equation which expresses the variation of the electromotive force with the temperature.

3. By a graphical method based upon first order differences, the temperature coefficients of electromotive force have been computed, as well as the partial molal heat content decrease of transfer from the concentrated to dilute solutions. This quantity is negative at the lower temperatures and becomes less negative as the temperature rises, reaching zero and assuming positive values in the vicinity of 40°. Since this change takes place uniformly, positive values are to be expected at the higher temperatures. If this is the case, then the activity coefficient will pass through a maximum and decrease with increasing temperature.

4. The activity coefficients at 0, 25 and 40° have been computed by Hückel's equation.

5. Accurate values of the activity coefficients at 0, 5, 10, 15, 20, 25, 30, 35 and 40° have been computed. At constant composition, they increase somewhat with the temperature and reach a maximum at about 40°.


NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# ERRORS INVOLVED IN THE DETERMINATION OF MINUTE AMOUNTS OF SODIUM BY THE MAGNESIUM URANYL ACETATE METHOD

BY EARLE R. CALEY

RECEIVED JULY 20, 1931 PUBLISHED FEBRUARY 5, 1932

In former papers in this series[1] attention was directed almost entirely to the errors involved in the direct determination of amounts of sodium ranging from one milligram upward. As far as the writer is aware, no systematic experiments have been made on the determination of smaller amounts than this by the particular procedure considered here. Due to the fact that the method has been applied to the determination of amounts of sodium below one milligram in various materials, it seemed advisable to make a systematic series of analyses in order to determine the errors in-

[1] (a) Caley and Foulk, THIS JOURNAL, **51**, 1664–74 (1929); (b) Caley, *ibid.*, **52**, 1349–53 (1930); (c) Caley and Sickman, *ibid.*, **52**, 4247–51 (1930).

herent in such estimations. In the following experiments the general procedure outlined in previous papers was followed using as a reference standard a carefully prepared solution of sodium chloride each cubic centimeter of which was equivalent to 0.10 mg. of sodium. Special modifications of the general method, used for experimental purposes in the following test analyses, are given in the proper places. It should be mentioned here, however, that in these determinations the precipitates were in all cases collected and weighed in medium-porosity, sintered-glass filtering crucibles instead of in Gooch crucibles as previously recommended. For this particular precipitate the use of glass crucibles has been found to lead to greater accuracy and convenience, especially the latter, since the salt can be dissolved out by simple washing with water leaving the vessels, after drying, unchanged in weight and ready for the next determination.

**Precipitation with Regular Reagent.**—In the first series of experiments, the results of which are shown in Table I, a 5-cc. volume of solution containing the stated amount of sodium was taken for each determination, 100 cc. of magnesium uranyl acetate reagent[1c] was added and the determination was completed in the usual way with particular regard to the condition of vigorous motor stirring which was found especially essential to the initiation of the separation of the triple acetate precipitate in these experiments involving such small amounts. Due to the delay sometimes encountered before precipitation began, the stirring time in all these determinations was extended to one hour. The results shown are not from selected determinations but are all the values obtained in one set of experiments. When it is considered that this is not intended as a micro-method it will be seen that the results obtained down to and including the 0.20 mg. quantity are, in general, satisfactory with the possible exception of the first value for the 0.30 mg. amount. It was found that amounts of sodium less than 0.20 mg. cannot be determined by the general method previously recommended.

TABLE I

DETERMINATIONS OF MINUTE AMOUNTS OF SODIUM

| Reagent used | Sodium present, mg. | Ppt., mg. | Sodium found, mg. | Error, mg. | Reagent used | Sodium present, mg. | Ppt., mg. | Sodium found, mg. | Error, mg. |
|---|---|---|---|---|---|---|---|---|---|
| Reg. | 0.50 | 29.1 | 0.45 | −0.05 | Sat. | 0.20 | 11.2 | 0.17 | −0.03 |
| Reg. | .50 | 36.9 | .56 | + .06 | Sat. | .20 | 17.4 | .27 | + .07 |
| Reg. | .50 | 31.9 | .49 | − .01 | Sat. | .20 | 16.4 | .25 | + .05 |
| Sat. | .50 | 37.3 | .57 | + .07 | Reg. | .10 | 2.6 | .04 | − .06 |
| Sat. | .50 | 38.3 | .59 | + .09 | Reg. | .10 | 2.5 | .04 | − .06 |
| Reg. | .30 | 13.6 | .21 | − .09 | Sat. | .10 | 1.7 | .03 | − .07 |
| Reg. | .30 | 21.2 | .32 | + .02 | Sat. | .10 | 3.5 | .05 | − .05 |
| Reg. | .20 | 11.4 | .17 | − .03 | Sat. | .10 | 7.2 | .11 | + .01 |
| Reg. | .20 | 13.3 | .20 | .00 | Sat. | .10 | 2.6 | .04 | − .06 |
| Reg. | .20 | 15.0 | .23 | + .03 | | | | | |

**Precipitation with Saturated Reagent.**—In view of the fact that the usual procedure was found to fail at a certain point, it was thought that a more concentrated reagent would bring about the quantitative precipitation of lower amounts of sodium notwithstanding the large total volume of solution involved. A reagent of the composition given below was therefore prepared, the two solutions being formed and mixed in the usual manner.

| Solution A | | Solution B | |
|---|---|---|---|
| Uranyl acetate ($2H_2O$) | 100 g. | Magnesium acetate ($4H_2O$) | 700 g. |
| Glacial acetic acid | 60 g. | Glacial acetic acid | 60 g. |
| Water | to 1000 cc. | Water | to 1000 cc. |

Since this reagent is one of practically the maximum possible concentration, it is designated in the following experiments as saturated reagent. When used in a series of determinations similar to those first mentioned it is apparent, from the values shown in Table I, that the saturated reagent does not aid much in the quantitative precipitation of even 0.10 mg. of sodium and that it has the disadvantage of tending to make the results for the larger amounts high in value. The error in this direction caused by the use of the more concentrated reagent was found to be due largely to the difficulty of preventing slight supersaturation of the saturated reagent with triple acetate precipitate in the course of its preparation. It should be noted, however, that this highly concentrated reagent has been found to have practical application in cases where it is not possible to reduce the solution from a given sample to the required volume of 5 cc. or less. Experiments have shown that the addition of a suitable volume of saturated reagent to a larger volume of solution (not more than 10 cc.) gives values for sodium determinations made by this method that are as satisfactory as those obtained by the usual procedure. The first four experiments shown in Table II are illustrative of this point. The first two determinations indicate the low results obtained when an attempt is made to estimate the

TABLE II

DETERMINATIONS UNDER VARIED CONDITIONS

| Reagent used | Solution volume, cc. | Sodium present, mg. | Ppt., mg. | Sodium found, mg. | Error, mg. |
|---|---|---|---|---|---|
| Reg. | 10 | 0.20 | 0.9 | 0.01 | −0.19 |
| Reg. | 10 | .50 | 23.5 | .36 | − .14 |
| Satd. | 10 | .20 | 11.8 | .18 | − .02 |
| Satd. | 10 | .50 | 34.6 | .53 | + .03 |
| Reg. | 1 | .10 | 5.6 | .09 | − .01 |
| Reg. | 1 | .10 | 5.9 | .09 | − .01 |
| Reg. | 5 | .20[a] | 11.5 | .18 | − .02 |
| Reg. | 5 | .50[a] | 40.3 | .62 | + .12 |
| Satd. | 5 | .20[a] | 25.3 | .39 | + .19 |
| Satd. | 5 | .50[a] | 43.4 | .66 | + .16 |

[a] 100 mg. of potassium also present.

given amounts of sodium by precipitation in a solution volume of 10 cc. with 100 cc. of regular reagent. The second pair of experiments shows the substantially correct results obtained with saturated reagent under the same conditions with respect to the amounts of sodium present and volumes used

**Determinations with Small Volumes of Solution and Reagent.**—By reducing the volume of solution employed in a determination, or, preferably, both the solution volume and the reagent volume in the same proportion, no difficulty is experienced in determining 0.10 mg. of sodium as illustrated by the two typical results shown in Table II, which were obtained by precipitation in 1.0 cc. of solution with 25 cc. of reagent. Even smaller amounts can be determined thus, so that in some cases the use of these smaller volumes may be a desirable procedure. In general, however, when operating on actual samples, the use of less than the recommended 5 cc. of solution and 100 cc. of reagent is often impractical due to interference caused by (a) the presence of sparingly soluble or soluble salts in amounts sufficient to render impossible the reduction of the solution to a smaller volume, (b) the presence of other than small amounts of potassium or (c) the simultaneous presence of sulfates and ammonium salts. Since the practical accuracy of direct methods using either magnesium uranyl acetate reagent or zinc uranyl acetate reagent hinges upon the avoidance of gross errors caused by the precipitation of any phase except the desired one, the increased sensitivity or accuracy obtained through the use of smaller volumes is reached only at the risk of errors greater than those intended to be avoided, especially when analytical samples of the usual weight are taken.

**Determinations in the Presence of Potassium.**—Since the case might often arise of determining these small weights of sodium in the presence of amounts of potassium many times larger, it was thought advisable to make experiments on this point although it has already been demonstrated that up to certain limits potassium does not, in general, interfere in this method. In Table II are shown four typical results that indicate the effect of an amount of potassium either two hundred or five hundred times the weight of sodium being determined. Apparently in such extreme cases the errors tend to be positive ones and they are more marked when saturated reagent is used, another reason for employing a reagent of the proper recommended concentration for determinations by this procedure. With less disproportionate ratios between the amounts of potassium and sodium correspondingly smaller errors occur and the results are then similar to those obtained with sodium present alone.

**Results on Actual Samples.**—Numerous test analyses have indicated that low percentages of sodium may be directly determined satisfactorily in various materials, the errors occurring being similar to those found in the

preceding experiments. Results obtained on a sample of reagent grade chromium sulfate (green modification) are shown in Table III. In order to place samples of this salt, having the given weights, in sufficiently small volumes of solution it was found necessary to dissolve them in hot water, then add the reagent with rapid mixing and finally complete the determinations in the usual way. This variation is often a necessary expedient when large samples must be taken. In the first set of experiments (A) in the table is recorded a series of results obtained by this procedure using varying sample weights, varying volumes of solution and the usual volume of reagent. In order to obtain some idea as to whether or not the satisfactorily duplicated results of series A were actually an accurate measure of the percentage of sodium in the material, a second series of determinations (B) was made by a method devised to test this point. In these an accurately measured volume of sodium chloride solution containing 1.00 mg. of sodium was added to each sample before precipitation. A weight of sodium magnesium uranyl triacetate corresponding to this amount of added sodium was then subtracted from the total weight of precipitate obtained in each case leaving the precipitate weights shown, which presumably represent the amounts of sodium originally present in the samples.

TABLE III

DETERMINATIONS OF SODIUM IN REAGENT GRADE CHROMIUM SULFATE

| Series | Sample, g. | Soln., volume, cc. | Ppt., g. | Sodium, % |
|---|---|---|---|---|
| | 1.0000 | 2–3 | 0.0106 | 0.016 |
| | 2.0000 | 4–5 | .0277 | .021 |
| A | 2.3170 | 5 | .0303 | .020 |
| | 2.3170 | 5 | .0266 | .018 |
| | 2.5000 | 5 | .0297 | .018 |
| | 0.9268 | 2–3 | .0125 | .021 |
| B | 0.9268 | 2–3 | .0110 | .018 |
| | 2.3170 | 5 | .0285 | .019 |
| | 2.3170 | 5 | .0281 | .019 |
| | 2.0000 | 5 | .0366 | .028 |
| C | 2.0000 | 5 | .0360 | .028 |
| | 1.0000 | 2–3 | .0141 | .022 |
| | 2.5000 | 5 | .0411 | .025 |

It will be seen that the results found in this manner agree satisfactorily among themselves and with those of the previous series, thus demonstrating that the values obtained by the direct method in the first instance were substantially correct. The final series of experiments shown in Table III were made to see if high results are liable to ensue when a reagent of excessively high concentration is employed for determinations made on actual samples and the results confirm the findings obtained on pure sodium chloride solutions recorded in the first part of the paper.

To determine whether or not different workers can obtain concordant values in the direct determination of low percentages of sodium, a sample of "C. P." crystallized aluminum sulfate of well-known make was examined independently by three analysts. Analyst A had previous experience with the procedure while the other two analysts had not used it before. The satisfactory concordance of results thus independently arrived at is demonstrated by the sets of values shown in Table IV.

TABLE IV

RESULTS OBTAINED INDEPENDENTLY ON THE SAME SAMPLE OF "C. P." ALUMINUM SULFATE BY DIFFERENT ANALYSTS

| Analyst | Sample, g. | Ppt., g. | Reported values for sodium: To third decimal, % | To second decimal, % |
|---|---|---|---|---|
| A | 2.0000 | 0.3043 | 0.233 | 0.23 |
| | 2.0000 | .3132 | .240 | .24 |
| B | 2.0000 | .3035 | .232 | .23 |
| | 2.0000 | .2992 | .229 | .23 |
| C | 1.5911 | .2378 | .229 | .23 |
| | 1.6830 | .2471 | .225 | .23 |

Determinations made on various other materials where this method is applicable have shown, in general, that satisfactory results are obtained as long as the quantity of sodium present is not less than 0.2 mg., a matter that can usually be regulated by the size of the sample taken.

## Summary

Experiments on pure solutions and on commercial samples have shown, in general, that small amounts of sodium may be determined satisfactorily by the direct magnesium uranyl acetate method as long as the amount present does not fall below 0.2 mg. Lesser weights may be determined in special cases by the use of unusually small volumes of solution and reagent.

The use of a more concentrated reagent leads to high results with the usual procedure and is not helpful in the quantitive precipitation of minute quantities of sodium.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

# BEHAVIOR OF OXALATE AND TARTRATE SOLUTIONS OF COLUMBIUM AND TANTALUM OXIDES[1]

BY F. H. EDMISTER AND G. G. ALBRITTON

RECEIVED AUGUST 10, 1931 PUBLISHED FEBRUARY 5, 1932

## Introduction

The freshly precipitated oxides or hydroxides of columbium and tantalum are appreciably soluble in aqueous solutions of oxalic and tartaric acids. This paper is chiefly confined with the nature of the resulting solutions.

The solvent action of these acids on the freshly precipitated hydrated oxides may theoretically be due to a simple reaction of double decomposition with the formation of the corresponding salt; to peptization of the hydroxide by the oxalate and tartrate ions; and by the formation of a complex. Russ[2] claims to have prepared a columbium oxalate to which he assigned the formula $Cb(HC_2O_4)_5$. He did not make a thorough investigation of the nature of the aqueous solution of this compound. It appears very unlikely that the columbium exists here as the simple cation since columbium and tantalum ions are so very rare and unstable in aqueous solutions. One might as well write the above formula as $H_5Cb(C_2O_4)_5$. According to Werner,[3] this compound may ionize into hydrogen ions and complex ions containing the metal. Evidence of this complex anion formation will be described in this paper.

## Experimental

**Preparation of the Pure Oxides.**—The starting material consisted of a partially purified mixture of columbium and tantalum oxides containing some iron and silica. The iron was removed as follows: after grinding, the oxides were dissolved in a hot concentrated solution of oxalic acid and the solution was filtered while hot through a Büchner funnel to remove any undissolved particles of silica. After cooling, the filtrate was diluted to twice its former volume. The columbium and tantalum were precipitated from this solution as the white amorphous columbic and tantalic acids upon the addition of an equal volume of concentrated hydrochloric acid. The whole contents was allowed to stand overnight, when the supernatant liquid was carefully decanted from the sediment. A little water was added and the contents stirred and filtered through a Büchner funnel. The residue was washed five times with hot 3 *N* hydrochloric acid and finally with water. It consisted of a mixture of columbic and tantalic acids, the iron being dissolved in the hydrochloric acid and passing into the filtrate. Although this procedure is satisfactory for the removal of iron, it is not recommended for a quantitative

[1] The material in this paper is an abstract of a thesis submitted by G. G. Albritton to the Graduate school of the University of North Carolina in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1931.

[2] Russ, *Z. anorg. Chem.*, **31**, 42 (1902).

[3] Werner, *J. Chem. Soc.*, **51**, 383 (1887).

recovery of the oxides of columbium and tantalum since some of these also dissolve in the hydrochloric acid.

**Separation of Tantalum from Columbium.**—The tannic acid method of Powell and Schoeller[4] was used to separate tantalum from columbium. This method of separation is based on the fact that tantalum is precipitated from an oxalic acid solution with tannic acid at a hydrogen-ion concentration too high for a precipitation of the columbium. Although this method of obtaining pure tantalum from a mixture of the oxides is satisfactory, it is not desirable for a rapid quantitative separation. There is a certain range of the hydrogen-ion concentration where columbium always begins to fall out before all the tantalum has precipitated. The precipitate formed within this range of hydrogen-ion concentration was rejected since a quantitative separation was not the object here. The tannic acid precipitates were ignited to the snow-white pentoxides.

**Behavior of the Oxalate Solution.**—Since the ignited oxides are insoluble in oxalic acid they were fused in silica crucibles with potassium bisulfate to a clear melt, according to the method of Schoeller and Powell.[4] After cooling, the fused mass was readily dissolved in a hot concentrated solution of sulfuric acid. Upon dilution and the addition of ammonia to neutralization, the white, gelatinous hydrated oxides of the metals precipitated. This unignited precipitate was readily and completely soluble in a boiling solution of oxalic acid.

The resulting solution behaved toward certain reagents as follows. Ammonia and the alkali hydroxides caused an incomplete precipitation of the metals as white amorphous precipitates. The tantalum being the least stable, is precipitated from this solution at a somewhat higher hydrogen-ion concentration than columbium. However, a quantitative separation was not realized when a mixture of the two oxides in oxalic acid solution was treated in this manner. In the presence of each other, the metals lose their individualities and behave in an almost identical manner.

The oxalate solution showed no evidence of a reaction toward organic acids, as citric, malic, succinic, benzoic, phthalic, salicylic and picric. The reagent acid crystallized in every case upon standing.

All attempts to prepare double oxalates with the heavy metals proved unsuccessful when the solution was treated with salts of $Fe^{++}$, $Fe^{+++}$, $Co^{++}$, $Ni^{++}$, $Hg^{++}$, $Ag^{+}$, $Hg^{+}$, $Cu^{++}$, $Al^{+++}$ and $Cr^{+++}$. In every case the oxalate of the reagent metal was precipitated.[1] [Russ claims to have prepared a double oxalate of columbium and barium to which he assigned the formula $Cb_2O_5 \cdot BaO \cdot 10C_2O_3$.]

**Behavior of the Tartrate Solution.**—Like oxalic acid and the alkali oxalates, tartaric acid and the alkali tartrates show appreciable solvent action on the freshly precipitated hydroxides of the two metals, which must be transferred to the tartrate solvent immediately after washing. The solubility of the hydroxides decreases rapidly when they are allowed to dry in the air. Furthermore the solvent action seems to be greatest if the solution is not heated to boiling but to a few degrees below. It may be mentioned here that solution takes place rather slowly as if dependent on an organic type of reaction rather than a reaction of the ionic type.

Differing from the oxalate solution, the metals are not precipitated in the least from the tartrate solution by ammonia and the alkali hydroxides. Strong mineral acids cause the metals to precipitate in the usual white amorphous form. Of the various salts of the heavy metals, only cobalt and calcium showed any evidence of forming complex tartrates with the metals. No activity was shown toward the above-mentioned organic acids. Acetone caused a quantitative precipitation of the metals in a fine white crystalline form, readily soluble in warm water. The resulting solution likewise proved to be inactive toward the various reagents.

[4] Powell and Schoeller, *Analyst*, **50**, 485 (1925).

Since the tartrate solution of the two metals showed very little activity, its exact nature became a question of interest. Experiments were carried out in an attempt to gain some knowledge of the manner in which the metals are held in solution.

An aqueous solution of tartaric acid was saturated with freshly precipitated columbium hydroxide and allowed to stand over sulfuric acid. The solution became viscous after a few days, and finally fine white tetrahedral crystals made their appearance. These crystals were found not to be tartaric acid. Upon prolonged standing they set to a hard crystalline mass which was very soluble in warm water. The resulting solution was inactive toward ammonia and the alkali hydroxides. This inactivity toward bases together with the formation of a viscous solution and a subsequent crystallization of microscopic crystals indicates the formation of tartrate complexes.

**Other Evidence of Complex Tartrate Formation.**—The change in the total hydrogen-ion equivalent of the solvent, tartaric acid, was determined by saturating an aqueous solution of 9.5356 g. of tartaric acid with the hydroxide and the subsequent titration with sodium hydroxide, using phenolphthalein as indicator. The tartaric acid solution was diluted to 250 cc. and aliquots of 25 cc. were titrated against 0.3826 *N* sodium hydroxide.

RESULTS

| | | |
|---|---|---|
| Tartrate solution, cc. | 25 | 25 |
| Base, cc. | 33.3 | 33.2 |
| Total hydrogen equiv. calcd. as free tartaric acid, g. | 9.5550 | 9.527 |

These results clearly show that there is no change in the total hydrogen equivalent of the tartaric acid. The dissolving of the hydroxide evidently does not involve a reaction of double decomposition in which hydrogen ions take part with formation of simple salt, or else if such a salt is formed it must be less stable than phenolphthalein, which seems improbable.[5]

The presence of a negative ion was determined electrolytically. Pure tartaric acid solution was placed in an anode compartment and the tartaric acid solution of the columbium pentoxide in the cathode compartment. The two compartments were connected by means of a salt bridge containing pure tartaric acid solution, the ends of which were plugged with cotton to prevent mechanical diffusion. The two platinum electrodes were connected to ten dry cells arranged in series. Three hours after closing the circuit the anode solution gave a decided test for columbium, and in twenty hours all the columbium had migrated to the anode.

Similar experiments were performed using tantalic acid instead of columbic. The behavior was the same.

These results indicate either a complex anion or an adsorption complex in which the metal is attached to the acid other than by the carboxyl group. Practically there is little difference between the two concepts.

**Preparation and Analysis of Tartra-columbic Acid.**—An aqueous solution of tartaric acid was saturated with $Cb(OH)_5$ by warming and stirring with an excess of the hydroxide for six hours. The undissolved hydroxide was filtered off and the filtrate allowed to stand over sulfuric acid. Fine white tetrahedral crystals formed after two days. Analysis showed the composition to be: Cb, 22.05%; $C_4H_4O_6$, 73.25%; $H_2O$ (crystallization), none. The results of this analysis give a ratio of two moles of tartrate to one mole of columbium and a total percentage of 95.33. Now if it be assumed that one OH group is attached to the columbium as in the compound $(C_4H_4O_6)_2CbOH$, the metal will then have a normal valence of five and the total percentage would be 99.51.

This formation of a compound of definite composition proves that the metal is not

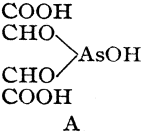
[5] Mellor, "Modern Inorganic Chemistry," Longmans, Green and Co., 1930, p. 286.

present in a dispersed condition. Evidently the hydroxide is acted upon by tartrates in a manner analogous to antimony, aluminum, arsenic, vanadium and other acidic oxides forming a class of compounds of the tartar emetic type.

**Comparison with Other Acidic Oxides.**—Clarke and Stallo,[6] in an investigation into the nature of the tartrates of antimony, came to the conclusion that tartar emetic ($KC_4H_4O_6SbO$) is a salt of the acid, $Sb(C_4H_4O_6)$. This acid, which he named tartra-antimonious acid, interacts, so he said, with the strong mineral acids with the precipitation of $H_3SbO_3$ according to the equation

$$C_4H_4SbKO_7 + HNO_3 + 2H_2O = C_4H_6O_6 + KNO_3 + SbH_3O_3$$

Henderson,[7] in a study of the action of certain acidic oxides on salts of hydroxy acids, prepared a sodium tartrarsenite by dissolving arsenious oxide in a hot solution of sodium hydrogen tartrate. Analysis showed the empirical formula to be $AsONaC_4H_4O_6 \cdot 2.5H_2O$. It appeared probable that this compound was the salt of tartrarsenious acid. This led him to the conclusion that the oxide enters into reaction with part or all of the alcoholic groups. According to this view the formula (A) was assigned to the so-called tartrarsenious acid. He failed to show, however, that the arsenic was tied up in a complex anion. No ion migration tests were made.

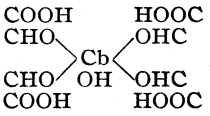


A

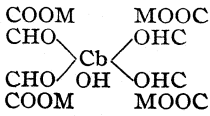
## Discussion of Results

As regards the constitution of the compounds formed by the action of tartaric acid on the hydroxides of columbium and tantalum, in the first place, it may be considered certain that they are not salts in which the radicals (HCbO) and (HTaO), play the part of metallic elements in replacing the hydrogen of one or more carboxyl groups. Moreover, the formation of these compounds by the action of hot aqueous solutions of the alkali tartrates and tartaric acid proceed very slowly. This mode of formation has a much closer resemblance to the organic type of reaction than to the production of metallic salts by the action of an acid on a basic oxide.

The structure of these compounds which agrees with the slow process of formation, composition and properties, is that the radicals (HCbO) and (HTaO) replace the hydrogen of the alcoholic hydroxyl groups, forming substances comparable to the acetyl and benzoyl derivatives of the hydroxy acids. If this view is accepted the following constitutional formulas for the compounds prepared in this investigation may be assigned as follows



Tartra-columbic acid



Alkali salt

[6] Clarke and Stallo, *Am. Chem. J.*, **2**, 319 (1880).

[7] Henderson, *J. Chem. Soc.*, **67**, 102 (1895).

where M represents the alkali metal. This conclusion is in accord with that of Henderson, concerning the action of the tartrates on arsenious oxide.

Ion migration test of the oxalate solution also showed that the metals migrate as anions. According to Russ[2] the oxides dissolve in oxalic acid forming definite compounds to which he assigned formulas. He did not test for the complex nature of these compounds. Since this investigation revealed the fact that the metals migrate as anions, it must be concluded that they are joined with the oxalate ions, forming complexes. It may be that columbium and tantalum form complexes with oxalic acid similar to chromium. According to Werner,[3] chromium forms with oxalic acid the complex chromo-oxalic acid, $H_6Cr_2(C_2O_4)_6$, where the chromium is united with the oxalate ion forming a complex anion. In agreement with this theory, columbium and tantalum would form the compound, $H_5M(C_2O_4)_5$, where M represents the metal.

## Summary

The freshly precipitated hydrated oxides of columbium and tantalum were found to be appreciably soluble in a hot aqueous solution of tartaric acid, forming compounds of the tartar emetic type.

Also it was found that the compounds formed when the oxides were dissolved in oxalic acid were not simple salts, but instead there were formed complexes. Ion migration tests showed that the metals united with the oxalate ion to form complex anions.

The oxalate and tartrate solutions of columbium and tantalum showed no activity toward various organic acids.

CHAPEL HILL, NORTH CAROLINA

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[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

# THE PREPARATION OF IODINE-FREE BROMINE

BY GEORGE M. KARNS AND H. C. DONALDSON

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The purification of most of the reagents used in the preparation of large samples for analysis for small amounts of iodine has been discussed at length by von Fellenberg[1] and Reith.[2,3,4] Some of the reagents used in smaller amounts, however, have not been dealt with so completely by these or other authors. Bromine, which is used as an oxidizing agent in one titrimetric method for the final determination, offers considerable chance for the introduction of iodine into the blank, C. P. bromine being frequently listed as containing 0.1% of that element. Saturated bromine water

[1] Von Fellenberg, *Ergebnisse Physiol.*, **25**, 194 (1926).

[2] Reith, Dissertation, Utrecht, July, 1929.

[3] Reith, *Biochem. Z.*, **216**, 250 (1929).

[4] Reith, *ibid.*, **224**, 223 (1930).

prepared from such bromine would contain a minimum of 40 gammas of iodine per cc. and if the bromine water used were prepared, as is often the case in the laboratory, by adding an excess to a bottle containing water, it could contain considerably more.

If iodine in bromine is present as iodine bromide, it should be possible to convert it to water-soluble iodic acid by treatment with water. Upon this assumption, an investigation was made of the effectiveness of successive washings in removing iodine from bromine. A sample of bromine, treated with iodine to bring its iodine content to 0.1% (the iodine content of C. P. bromine was usually found to be considerably below the manufacturer's figure), was washed successively with 500 cc. portions of water, using a mechanical shaker. Data obtained from iodine determinations upon the washings from a typical run are given in the accompanying table.

TABLE I

IODINE DETERMINATIONS

Initial weight of bromine, 453 g. Purified bromine obtained, 246 g.

| | Iodine per 100 cc. washings (gammas) | Total iodine removed (gammas) | Iodine to be removed subsequently |
|---|---|---|---|
| 1st washing, after 1 hour | 9320 | | |
| 1st washing, after 3 hours | 9640 | 48132 | |
| 2d washing, after 3 hours | 16.6 | 83.0 | 31.4 |
| 3d washing, after 1 hour | 1.8 | | |
| 3d washing, after 3 hours | 4.2 | 18.6 | 12.8 |
| 4th washing, after 3 hours | 1.0 | 4.9 | 7.9 |
| 5th washing, after 6 hours | 0.7 | 3.8 | 4.1 |
| 6th washing, after 24 hours | 0.5 | 2.5 | 1.5 |

Iodine remaining in bromine sample as estimated by the method described in the following paragraph less than 1.5 gammas.

That oxidizing agents other than bromine were being removed by the first washings was indicated by the fact that, upon boiling to remove bromine, cooling and adding excess potassium iodide, a shifting end-point was obtained when the solution was titrated with thiosulfate. This difficulty would be carried over to the actual determinations if the bromine water examined had been used and may account in part for the difficulties that have caused numerous investigators to abandon the oxidation titrimetric method for the colorimetric method in the micro-determination of iodine. Determinations were made on such samples by boiling off the bromine, reducing with acidified sodium sulfite, evaporating to dryness after the addition of potassium carbonate, and extracting with alcohol. The final determination of iodine was then made titrimetrically, as described above, using water from purified bromine as an oxidizing agent. As the washing was continued determinations made directly, and after reduction and extraction as described above, became identical. In the determination of iodine in the purified bromine sample, 100 cc. of bromine

was allowed to evaporate through a layer of water containing a small amount of sodium hypobromite. This method was chosen in preference to one which would introduce considerable amounts of other reagents after a control determination showed good recovery of iodine.

From the data in the table it is evident that bromine of sufficient purity for microchemical work can be prepared by the washing method. It is also evident from data on the third washing at the end of one and three hours, respectively, that considerable time must be allowed for the reaction between iodine bromide and water to take place. Water from the third washing, if separated from the bromine residue, would introduce less than 0.04 gamma of iodine into the sample per cc. of bromine water used. Saturated bromine water prepared from the bromine obtained at this stage would contain approximately one-twentieth of that amount.

## Summary

A method for the preparation of iodine-free bromine for use in the microanalytical determination of iodine is described.

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE MICHIGAN COLLEGE OF MINING AND TECHNOLOGY]

# THE SURFACE RELATIONS OF POTASSIUM ETHYL XANTHATE AND PINE OIL. I

BY C. C. DEWITT AND EDWIN E. ROPER

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During recent years the froth flotation method for the concentration of ores has made great progress, but an actual knowledge of the mechanism of the formation of the froth and the flotation of the metallic values by the admixture of potassium ethyl xanthate and pine oil is still lacking. A program of research has been instituted from which, it is hoped, a satisfactory explanation of the phenomena may result. This paper is a brief exposition of the methods used and the results obtained in the first stage of the investigation. Generalization in the field as a whole is reserved for later papers, when more complete data on the surface relations of these materials will be available. In this report data on the surface relations of solutions of potassium ethyl xanthate and pine oil are presented, the relative values of the various data are discussed, and problems are suggested for future solution.

The surface tension of the potassium ethyl xanthate solutions was measured by the methods of Ferguson and Dowson and the interfacial tension of the xanthate–pine oil system by the method of Bartell and Miller. A series of parallel determinations was carried out on sodium car-

bonate solutions in order to determine the effect of the hydroxyl ion. Several relevant secondary phenomena were observed, the significance of which will be more thoroughly investigated, and reported in later papers.

**Purification of Materials.**—The xanthate as purchased was a supposedly pure product, but upon examination it gave a distinct carbon disulfide odor and showed a brownish-yellow color, and also heterogeneous lumps of darker shade; these lumps were picked out and discarded as unfit material. Considerable effort was expended in working out a suitable method of purification. Foster[1] states that recrystallization from acetone–benzene, and from acetone–petroleum ether mixtures, or from alcohol can be used to obtain pure crystals of xanthates. It is to be noted that Foster prepared his xanthates from pure materials and proceeded immediately to purification. We followed his method on a small scale and obtained a good product. For large quantities of material this method of recrystallization did not prove applicable; the xanthate thus obtained was found to decompose so readily that the product was not much purer than the original. A precipitation method was devised whereby the xanthate was exposed to the solvent and to the atmosphere for a short time only.

Because of the high specific volume of the xanthate and the large amounts of solvents necessary, a batch of 100 g. was about the maximum amount that could be handled conveniently. One hundred grams of xanthate was added to 1000 cc. of warm acetone (40°) on a water-bath and stirred for a few minutes; some of the xanthate did not dissolve—in fact, this undissolved portion appeared to be quite different from the rest, being but slightly soluble even in an excess of boiling acetone. No attempt was made to examine this insoluble portion; it was filtered off through a hot water funnel and discarded.

To the cold filtrate 4000 cc. of benzene was slowly added, with stirring, and the precipitate was filtered out on a Büchner funnel, with the aid of suction. This precipitate was then dissolved in 500 cc. of acetone and 5000 cc. of petroleum ether quickly added, with no stirring. The precipitate thus obtained was again recovered by filtration through a Büchner funnel and was washed with several 50-cc. portions of petroleum ether (40–50°). It was then transferred to a vacuum desiccator containing a small beaker of concentrated sulfuric acid and a small amount (15–20 g.) of recently heated active charcoal on a watch glass, and was kept under a vacuum of a millimeter of mercury for at least twelve hours. At the end of this time, the acid and the charcoal were exchanged for fresh portions and the xanthate was stored in the desiccator. This purified product had no odor, was of a light cream color, and gave a colorless dilute solution in water. The degree of purity of this xanthate was established by comparative determinations of sulfur content: Carius method: S calcd. 40.01; S found, 39.98. The decomposition point of the purified material on heating was 200 ± 0.3°. Subsequent batches of xanthate purified in the same manner were checked as to purity by the surface tension values of solutions and the density of these solutions. The decomposition point of the xanthate was found to be easily reproducible.

The pine oil, obtained from the Hercules Powder Company, was a triply distilled commercial product with a clear, light yellow color. This material consisted mainly of a mixture of pinene, fenchyl alcohol, α-terpineol, dipentene, terpinolene and borneol. No attempt was made to purify it other than to remove most of the water. This was accomplished by allowing the oil to stand for one month or longer in contact with granular, anhydrous calcium chloride. The density dropped no lower after this interval, indicating that all the water which could be removed by this method was taken out.

[1] Foster, "Preparation of Xanthates and Other Organic Thiocarbonates." University of Utah, Tech. Paper No. 2, 1928.

All other materials were purchased as C. P. reagents and were purified by recrystallization methods.

**Thermometric Standards.**—Thermometers used were checked against the melting points of triply distilled water, purified naphthalene, benzoic acid, urea, diphenylurea and anthracene. The values of these melting points were taken from "International Critical Tables."

**Determination of Surface Tension.**—The selection of a simple and reliable method of determining surface tension presents considerable difficulty. The capillary rise method, as has been shown by other workers[2] in this field, is difficult to apply properly. Its great disadvantage is in the difficulty of obtaining even a short length of capillary tubing with a uniform bore; Harkins and Brown[2b] examined 500 feet of capillary, and Richards and Carver[2c] a like amount before they found a short piece suitable to their needs.

The method of Ferguson and Dowson[3] was used in measuring the surface tension values reported in this paper. This method makes use of the fact that if a capillary tube is immersed vertically in the liquid for which the surface tension is to be evaluated and if the meniscus is forced down to the exact end of the capillary by applied pressure, then the value of the surface tension, $\gamma$, may be expressed in terms of six factors: (1) the height of the manometric liquid, $h_m$; (2) the density of the manometric liquid, $\rho_m$; (3) $r'$, the radius of the capillary at the extreme end of the immersed portion; (4) $\rho_c$, the density of the liquid under investigation; (5) $h_c$, the depth of immersion of the capillary; and (6) the contact angle, $\theta$, between the experimental liquid and the capillary.

Some contact angles have been measured and found to be zero for a water–glass interface. A contact angle of 6° will give rise to an error of about 1% in the value of the surface tension of water. The most concentrated xanthate solution used was 1.3 molal, and if the contact angle were formed by the addition of the solute, it would probably necessitate but a small correction.

For this type of apparatus, Ferguson and Dowson have given the mathematical relationship connecting surface tension and the six factors mentioned. However, their final equation, while correct, is not clear in its definition of terms nor in the assumptions made. In particular, their densities as written should mean the density of the liquid minus the density of the saturated vapor.

According to Dr. N. E. Dorsey[4] the equation for the surface tension should be

$$\gamma = \frac{g\,r'}{2}\left[(\rho_m - \sigma_m)h_m - (\rho_c - \sigma_c)h_c\right] + \frac{1}{6}r'^2(\rho_c - \sigma_c)g \qquad (1)$$

[2] (a) Richards and Coombs, THIS JOURNAL, **37**, 1656 (1915); (b) Harkins and Brown, *ibid.*, **41**, 502 (1919); (c) Richards and Carver, *ibid.*, **43**, 638 (1921).

[3] Ferguson and Dowson, *Trans. Faraday Soc.*, **17**, 384 (1921).

[4] Dr. N. E. Dorsey, private communication.

in which $g$ is the acceleration due to gravity, $\sigma_c$ is the density of the vapor immediately over the meniscus in the capillary, and $\sigma_m$ is the density of the vapor immediately over the meniscus in the arm of the manometer. The remaining symbols have been defined.

In all of our determinations water was used as the manometric liquid and since the vapor pressure lowering due to the solute is negligible (mole fraction of xanthate at the highest concentration is 0.02), we may use as an approximation

$$\sigma_c = \sigma_m \tag{2}$$

To neglect $\sigma_m$ will limit our accuracy to about 0.5% at values of $\gamma = 70$ dynes per centimeter. Since this order of accuracy was suitable, $\sigma_m$ was entirely neglected. In the second term on the right-hand side of (1) $r'^2 \sigma_c$, being of the second order, may be neglected without influence on the results.

The simplified equation now becomes

$$\gamma = \frac{g\,r}{2}\,[\rho_m h_m - \rho_c h_c] + \frac{1}{6}\,r^2\,\rho_c g \tag{3}$$

This is the equation which Ferguson and Dowson give and is that which Edwards[5] used to calculate his results.

In equation (3) it will be noticed that we have substituted $r$ for $r'$, where $r$ is the "effective" radius of the immersed end of the capillary. This change was adopted for our convenience; it will be explained later in connection with standardization.

For ease in computing values of $\gamma$ from experimental data we can write

$$\gamma = A\Sigma(\rho h) + B\rho_c \tag{4}$$

where

$$A = \frac{g\,r}{2};\ \Sigma(\rho h) = (\rho_m h_m - \rho_c h_c);\ B = \frac{g\,r^2}{6} \tag{5}$$

It can be seen that $A$ and $B$ are constants for a given apparatus.

The apparatus in its final form is shown in Fig. 1. It consisted of Pyrex glass with all joints fused, except the short length of rubber tubing K. The beaker, D, was at least 45 mm. inside diameter; all the experimental liquid was immersed in the thermostat, with the capillary tip 4–5 cm. below the experimental liquid surface. The manometer, the air reservoir and the connecting lines were all immersed in the thermostat liquid wherever possible. The pressure necessary to force down the meniscus was applied to the tip through a column of water NAKF and was varied by raising or lowering the reservoir N by means of the rod L, which operated a rack and pinion gear. The arm LP for operating the elevating mechanism of the reservoir, N, extended back to the cathetometer, a distance of about 150 cm., in order that the pressure might be varied, and the result observed through the cathetometer telescope. This connecting arm, operating in bearings at 75-cm. intervals, provided a means of delicate adjustment of the pressure.

Stopcock B was used in cleaning the tip. During this cleaning, stopcock A was closed and the open arm of the manometer was plugged with a cork. When a deter-

[5] Edwards, *J. Chem. Soc.*, **127**, 744 (1925).

mination was to be made, the positions of the stopcocks were reversed and the cork removed.

The aquarium thermostat had two plate glass sides and contained 48 liters of a colorless mineral oil (Finol). In Fig. 1, a cross sectional view is given. The remaining walls of the tank were of sheet copper, with a 5-cm. layer of insulating material on the outside.

Both the copper tank and the stirrers and metal stands within the bath were grounded through a switch. After equilibrium of the meniscus was attained the switch was opened to discover whether any electrical effect on the meniscus could be observed. No disturbance of the meniscus level could be observed when the switch was left open while equilibrium was being established and then closed.

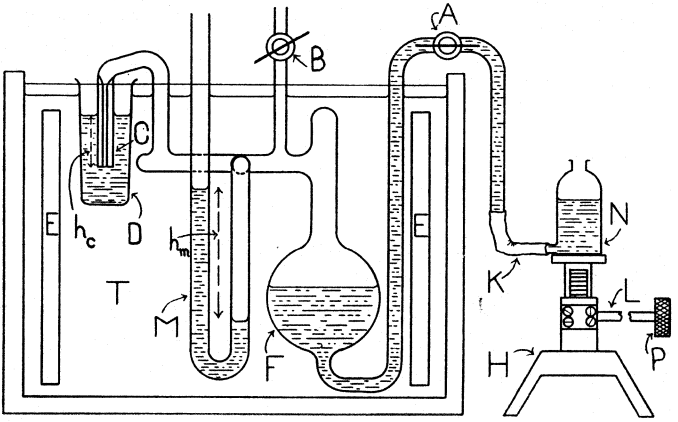


Fig. 1.—Ferguson apparatus for determining surface tension by balanced pressure.

The temperature of the bath was set at 25°. Near the center of the bath variations of 0.01° were rare.

The capillary tip C was kept immersed in a chromic anhydride-sulfuric acid mixture when not in use; just before a determination the tip was thoroughly cleaned and immersed in the experimental liquid contained in D. (The complete glass apparatus could be moved vertically on a slide.)

After thermal equilibrium was attained, air, forced out of the tip by the raising of N, gave a fresh surface; the meniscus was then pulled into the capillary for about a millimeter to wet the walls and was then forced down to the end of the tip. The horizontal cross hair of the cathetometer telescope was set on the end of the tip. After drainage had ceased, the final adjustment of bringing the meniscus into coincidence with the cross hair was accomplished, and $h_c$ was measured. Next $h_m$ was measured, and finally each height was checked.

Tip No. E was standardized by finding the $\Sigma(\rho h)$ in equation (4) for pure water at 25°. The values were substituted in equation (3) and the resulting quadratic was solved for $r$, the value of $\gamma$ being taken as 71.97 dynes per cm.[6] The mean of six determinations gave the average value of $r$ as 0.017915 cm. with a maximum deviation of 0.2%. This method gives the value of $r$, while a comparative reading would give $r'$. The quantity $r$ can be given the significance of a mean, integrated radius, which,

[6] "International Critical Tables," Vol. IV, p. 447.

when substituted in equation (3), gives a correct value of ($\gamma = \pm 0.5\%$), but this $r$ is not necessarily the actual radius that would be obtained by physical measurements.

As a check on this value of $r$, the same procedure was carried out using purified benzene as the experimental liquid, the value of $\gamma$ for benzene at 25° being taken as 28.22 dynes,[6] and the average value of $r$ was found to be 0.01792 cm., with a maximum deviation of 0.2% from the mean.

Using the value of 0.01792 cm. for $r$, we calculated the values of the constants $A$ and $B$ in equation (4)

$$\gamma = 8.7898\ \Sigma(\rho h) + 0.0526\ \rho_c$$

The value of $g$ for this locality has been found to be about 981 dynes. The values for the densities of water and benzene were taken from "International Critical Tables."

**Determination of Interfacial Tension.**[7]—The method of Bartell and Miller[7] was used for determining the tension at the interface of the two liquid phases. The method is adequately treated by the authors in their original article, which can be consulted for details.

The radii of the cell capillaries were standardized with water and as a check the interfacial tension of the system benzene–water at 25° was determined. A maximum deviation of +0.17% from the accepted value of 34.56 dynes per cm. was observed for cell No. 2, and a deviation of −0.17% for cell No. 1.

The density of the solutions was determined by the pycnometer method, using 25-cc. pycnometers. These were placed in a smaller water-bath which was then immersed in the main oil-bath. No difficulty was experienced in obtaining results accurate to the fourth decimal place.

## Results

The values of $\gamma^{25}$ for xanthate solutions were determined; these data are given in Table I and are presented graphically in Fig. 2. On the same graph is plotted the surface tension of sodium carbonate solutions, the values being taken from "International Critical Tables."

TABLE I

THE SURFACE TENSION OF AQUEOUS POTASSIUM ETHYL XANTHATE SOLUTIONS AT 25°

| $m$, molality of xanthate | $N_2$, mole fraction of xanthate | $d_4^{25}$, g./cc. | $\gamma^{25}$, dynes/cm. |
|---|---|---|---|
| 0.0000 | 0.0000 | 0.9971 | 71.97 |
| .2700 | .0048 | 1.0145 | 71.36 |
| .6510 | .0116 | 1.0374 | 69.44 |
| .9430 | .0167 | 1.0512 | 68.10 |
| 1.3020 | .0229 | 1.0679 | 65 95 |

The values obtained for the interfacial tension of pine oil–xanthate solutions represent mutual saturation to such an extent as saturation took place at the interface after the two phases had been in the cell. Attempting

[7] Bartell and Miller, THIS JOURNAL, 50, 1961 (1928).

mutual saturation earlier gave rise to an emulsion. The character of each phase adjacent to the interface in the cells indicated saturation. A slow change of tension with time was noted but was not investigated thoroughly.

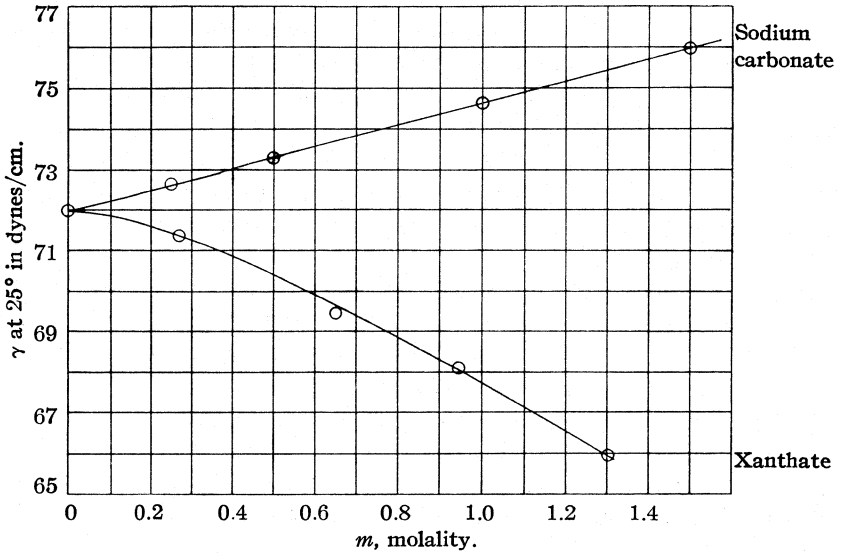


Fig. 2.—Surface tensions of $Na_2CO_3$ and $KS(S)COC_2H_5$ at 25°; values for $Na_2CO_3$ from "I. C. T.," Vol. IV, p. 446.

The values given for $S$ represent the interfacial tension at zero time of contact of the two phases, since they are either the values obtained as soon as

TABLE II

INTERFACIAL TENSION OF PINE OIL AGAINST AQUEOUS POTASSIUM ETHYL XANTHATE SOLUTIONS AT 25°

| $m$ molality of xanthate | $d_4^{25}$, density of xanthate solutions | $S_{2,s}$, interfacial tension (dynes/cm.) |
|---|---|---|
| 0.00000 | 0.9971 | 10.88 |
| .0370 | .9992 | 11.63 |
| .0750 | 1.0018 | 11.97 |
| .1110 | 1.0041 | 12.19 |
| .1470 | 1.0064 | 12.36 |

TABLE III

INTERFACIAL TENSION OF PINE OIL AGAINST AQUEOUS SODIUM CARBONATE SOLUTIONS AT 25°

| $m$ molality of $Na_2CO_3$ solution | $d_4^{25}$, density of $Na_2CO_3$ solution | $S_{2,s}$, interfacial tension (dynes/cm.) |
|---|---|---|
| 0.0000 | 0.9971 | 10.88 |
| .0228 | .9996 | 10.16 |
| .0584 | 1.0034 | 9.75 |
| .1480 | 1.0128 | 8.88 |

The density of our sample of dried pine oil was 0.9279 g./cc.

possible after the cell was filled or the values obtained by the extrapolation of the $S$–time curve to zero time. The value of $dS/dT$ was negative for the xanthate–pine oil system and positive for the sodium carbonate–pine oil system. Tables II and III give the collected data, both sets being graphed on Fig. 3.

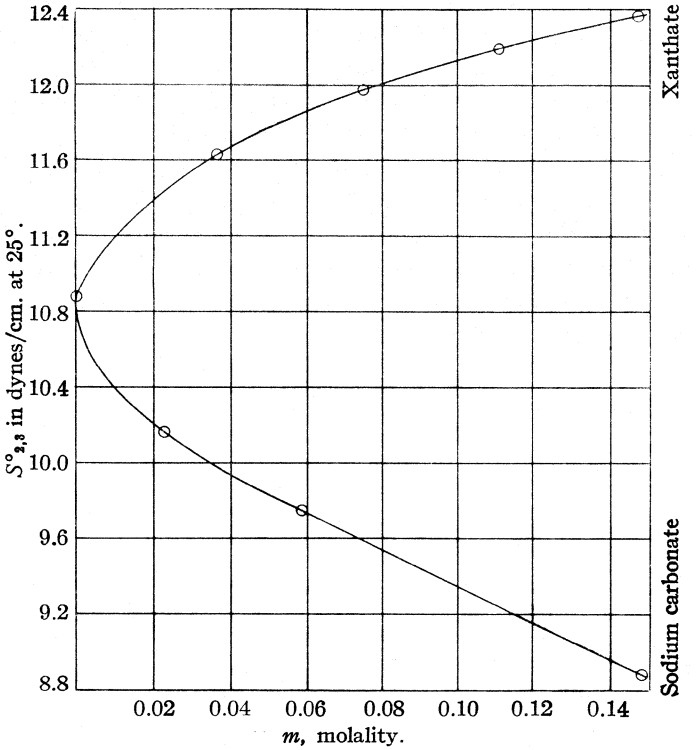


Fig. 3.—Interfacial tension of aqueous solutions against pine oil at 25°.

In the initial stage of the experimental work it was noticed that the xanthate solutions changed color upon standing. In view of this, all determinations were made upon freshly prepared solutions. In order to investigate the effect upon the physical properties being measured, these properties were determined on different solutions over a period of a month. Table IV shows some typical results obtained on one solution.

Thus it can be seen that the appearance changes markedly after one day of standing, the density shows practically no change within the limits of experimental error, and the interfacial tension against pine oil shows a slight minimum at the time of turbidity, or translucence.

This translucent state became evident from eight to forty-eight hours

TABLE IV

CHANGES IN POTASSIUM ETHYL XANTHATE SOLUTIONS, 0.037 MOLAL, KEPT IN A GLASS-STOPPERED PYREX FLASK AT ROOM TEMPERATURE

| Interval after preparation, days | Appearance | Odor | $d_4^{25}$, g./cc. | $S_{2,3}$, dynes/cc. |
|---|---|---|---|---|
| 0 | Clear, very light yellow | None | 0.9992 | 11.97 |
| 1 | Translucent, yellow | None | .9990 | 11.38 |
| 8 | Clear, brownish-yellow | $CS_2$ | .9989 | 11.68 |
| 28 | Clear, brownish-yellow | $CS_2$ | .9990 | 11.63 |

after the solution had been prepared, the time being roughly proportional to the concentration of the xanthate solution. This cannot be due to the presence of residual solute, for then it should make its appearance upon preparation of the solution, and should be permanent, since the xanthate solution was not removed from the flask, except for the amounts necessary for determinations. No separation either of a liquid or a solid phase was observed. An examination of the $P_H$ values at different times showed that there was a distinct and continuous change in hydrogen-ion concentration as the change proceeded.

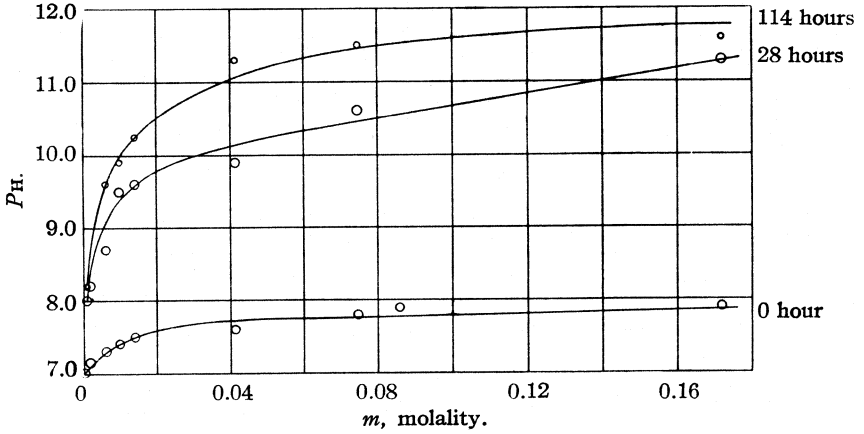


Fig. 4.—Variation of $P_H$ of xanthate solution.

Solutions of different concentrations were placed in the thermostat at 25° and the hydrogen-ion concentration determined at intervals by means of a roulette comparator. At the end of 114 hours the more concentrated solutions were so highly colored that the colorimetric determination was but a very rough estimate of the $P_H$ value. The results are shown graphically in Fig. 4.

## Discussion of Results

The xanthate readily hydrolyzes in aqueous solution, since $C_2H_5OC(S)SH$ can be classed as a weak acid.[8] Other reactions probably occur,

[8] Halban and Kirsch, *Z. physik. Chem.*, **82**, 325 (1913); Halban and Hecht, *Z. Electrochem.*, **24**, 65 (1918).

since ethyl xanthic acid is readily decomposed at room temperature, and its low boiling point, 24°, together with its slight solubility in water, 0.02 mole per liter, would tend to shift the hydrolysis toward the acid side of the reaction, which alone would probably account for the observed change in $P_H$ with time.

Sodium carbonate solutions were studied in experiments parallel to those of xanthate solutions to show the effect of the hydroxyl ion on $\gamma$ and $S_{2,3}$, resulting from the alkali salt of a weak acid.

According to the deductions from the modified Gibbs equation

$$\Gamma = -\frac{m}{RT}\left(\frac{d\gamma}{dm}\right)_T$$

if $d\gamma/dm$ is negative, the surface or interfacial concentration of the solute, $\Gamma$, is positive, and *vice versa*. Recently the assumptions made in deriving this equation have been questioned.[9] Under any circumstances the activity of the solute should be used in place of its molality, so that the equation would be: $\Gamma = d\gamma/RT\ d\ln a$. Preliminary measurements of freezing point lowerings have been made, and the activity for xanthate solutions has been evaluated from these measurements; but before the results may be considered as final, the work is to be repeated. Qualitative results obtained from the use of the Gibbs equation are summarized in Table V.

TABLE V

SIGN OF $\Gamma$, SURFACE CONCENTRATION OF SOLUTE AT DIFFERENT INTERFACES

| Liquid 2 | Air–liquid 2 interface ($\gamma$) | Pine oil–liquid 2 interface ($S_{2,3}$) |
|---|---|---|
| K Et X (aq.) | Positive | Negative |
| $Na_2CO_3$ (aq.) | Negative | Positive |
| Pine oil (aq.) | Positive[a] | 0 |

[a] Fahrenwald, *Min. Sci. Press*, **123**, 227 (1921); Gaudin, Univ. Utah Tech. Paper No. 1 (1928).

From Table V it can be seen that, qualitatively, xanthate solutions behave quite oppositely to sodium carbonate solutions. From this it would appear that the hydroxyl ion resulting from hydrolysis cannot be wholly responsible for the results obtained from xanthate solutions.

Harkins and his collaborators[10] have studied, among other substances, the surface relations of water, carbon disulfide and ethyl mercaptan. Their results show that the (SH) part of the mercaptan molecule is more polar than the divalent sulfur atom; that when the mercaptan lies in contact with water, most of the (SH) groups are turned toward the polar phase—in this instance, water; and that when these groups are pulled

[9] Harkins and McLaughlin, THIS JOURNAL, **47**, 2086 (1925); Harkins and Gans, "Colloid Symposium Monograph," **6**, 17 (1928); McBain and Davies, THIS JOURNAL, **49**, 2230 (1927).

[10] Harkins, Clark and Roberts, *ibid.*, **42**, 707 (1920).

from the water, the polarity of the group is evident in the high value of adhesional work[11] of the mercaptan and in the smaller value for carbon disulfide, which is 12.7 ergs less.

On account of the SH group the behavior of $C_2H_5OC(S)SH$ should be somewhat similar to that of mercaptan, and also to that of carbon disulfide, since the divalent sulfur atom is also present. The ether type of bonding should give rise to strong non-polar characteristics. Hence this molecule should show a non-polar end ($C_2H_5$—O—C—), and a polar end, —CS—S—H. The combined effect of these four groupings—hydrocarbon, ether, disulfide and mercaptan—is rather difficult to predict.

At the surface of an aqueous solution of xanthate, the polar end will extend into the water phase, while the non-polar end will extend into the vapor phase. Theoretically, the concentration at the surface should be greater than in the bulk of the liquid; such is shown to be the case in Table V.

At the surface of a xanthate–pine oil system, the polar end will extend into the aqueous phase and the non-polar end will certainly be repulsed by that phase. Whether it will be attracted by the pine oil phase should depend upon the polarity of that phase. From a consideration of the components of pine oil, it would seem that a majority of non-polar substances predominates. If this is a correct assumption, the concentration of xanthate should be greater in the interface than in either of the two phases, pine oil and water. The indications from the $S$–$m$ curve show that $dS/dm$ is positive, and therefore the interfacial concentration of the xanthate is less than in the bulk of the aqueous phase. However, we do not know whether we are measuring the interfacial concentration of the potassium salt, the acid or the ions; the most plausible assumption is that we are measuring the combined effect of all three.

Hence, no attempt can be made to draw logical conclusions until more interfacial data are obtained. The effect of hydroxyl ion on interfacial tension between xanthate solutions and each pure component of pine oil as the non-polar phase, must be determined. This investigation is being carried on at present.

## Summary

1. The surface tensions of aqueous potassium ethyl xanthate solutions up to 1.3 molal have been measured at 25°, and $d\gamma/dm$ has been found to be negative.

2. The interfacial tension of dilute solutions of potassium ethyl xanthate against pine oil has been measured at 25°, and $dS/dm$ has been found to be positive.

3. It has been shown by means of parallel experiments with sodium

[11] Harkins and Cheng, THIS JOURNAL, 43, 35 (1921).

carbonate, that the hydroxyl ion resulting from the hydrolysis of the alkali salt of a weak acid cannot be wholly responsible for the observed results.

HOUGHTON, MICHIGAN

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE MICHIGAN COLLEGE OF MINING]

# THE SURFACE RELATIONS OF THE COMPONENTS OF PINE OIL AND OF POTASSIUM ETHYL XANTHATE. II[1]

BY C. C. DEWITT AND R. F. MAKENS

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The object of the work here reported is two-fold: to determine the surface relations of aqueous solutions of various components found in pine oil and to extend the work of DeWitt and Roper[2] on the surface tensions of aqueous potassium ethyl xanthate solutions. The data on surface tension will be used in conjunction with wettability experiments now in progress in this Laboratory. The data on the pine oil components can also be used as a measure of the value of the several constituents as frothers for ore flotation purposes.

All surface-tension determinations were made with a drop-weight apparatus, and all interfacial tension determinations with a drop-volume apparatus. Both sets were constructed by Mr. Richard Kittel of the Kent Chemical Laboratories, the University of Chicago, under the supervision of Dr. Gans.

The drop-weight apparatus was similar to that used by Gans and Harkins[3] except for the method of raising and lowering the supply bottle. Each determination consisted of a run of thirty drops followed by a run of five drops. The difference represented the weight of twenty-five drops. Two determinations were made at each concentration. This procedure is that suggested by Harkins and used in the experiments reported in his latest paper on the subject, except that he made twenty-drop instead of thirty-drop runs. The equation used in the calculation of the surface tension is

$$\gamma = \frac{w\,g\,\phi}{2\,\pi\,r}$$

where $\gamma$ is the surface tension, $w$ is the weight of one drop, $d$ is the density of the liquid phase, $r$ is the radius of the tip, $v$ is the volume of the drop calculated from the weight and density and $\phi$ is the reciprocal of a function of $r/v^{1/3}$.

The functions were taken from the work of Harkins and Brown.[4]

[1] These papers were presented at the Spring Meeting of the American Chemical Society at Indianapolis, Division of Physical and Inorganic Chemistry.

[2] DeWitt and Roper, THIS JOURNAL, **54**, 444 (1932).

[3] Gans and Harkins, *ibid.*, **52**, 2290 (1930).

[4] Harkins and Brown, *ibid.*, **41**, 519 (1919).

The interfacial tension apparatus was very similar to that constructed by Harkins and Humphrey.[5] The equation for calculating the interfacial tension is

$$\gamma_{12} = \frac{v\,(d - d)\,g}{2\,\pi\,r}\,\cdot$$

where $\gamma_{12}$ is the interfacial tension of the liquid–liquid interface, $v$ is the volume of the drop, $d$ is the density of the upper liquid, $d'$ is the density of the lower liquid, $r$ is the radius of the tip, $\phi$ is a function of the quantity $r/v^{\frac{1}{3}}$.

The table of correction functions was the same as that applied in the drop weight method.[6] All density determinations were made with ordinary 25-ml. pycnometers. The usual precautions necessary for accurate work were observed. The temperature was maintained at 25.00 ± 0.015° in a water-filled glass thermostat.

**The Materials Used.**—The benzene for the standardization of the drop-weight and the drop-volume apparatus was a thiophene-free C. P. grade obtained from Eimer and Amend. It was cooled to 0°, and, after it had solidified as much as possible, the mother liquor was poured off. The solid melted at 5.5°, and was then cooled and resolidified. The mother liquor was poured off, and the benzene crystals were twice distilled in a 76-cm. fractionating column. The boiling point was now constant. The middle fraction was used.

The water for standardization work was purified according to the procedure followed by DeWitt and Roper,[2] and results similar to theirs were obtained. The Harkins drop-weight apparatus showed no detectable difference between the surface tension of the specially purified grade of distilled water and that of the ordinary laboratory grade. However, the specially purified grade was used for all standardization work.

Ordinary steam-distilled Yarmour pine oil was used with no further purification except that it was dried over anhydrous calcium chloride for a month—not an effective method of drying pine oil, as later distillation proved. The densities of two samples from different kegs were $d_4^{25}$ 0.92813 and $d_4^{25}$ 0.92833, respectively, after the drying. That pine oil is by no means constant in composition is indicated by Taggart[7] and by analysis made in this Laboratory.

The potassium ethyl xanthate used was purified by the method used by DeWitt and Roper. A Carius combustion to determine purity gave very satisfactory results.

The compounds found in pine oil vary to some extent with the wood or needles used. The compounds usually found in pine oil in appreciable amounts have been named by O. A. Pickett,[8] as α-terpineol, pinene, dipentene, terpinolene, borneol and fenchyl alcohol. A. Schorger[9] and R. H. Stevens[10] mention small amounts of camphor and other products.

[5] Harkins and Humphrey, THIS JOURNAL, **38**, 237 (1916).

[6] Harkins, "Colloid Chemistry," Alexander, The Chemical Catalog Co., New York, 1926, p. 259.

[7] Taggart, "Manual of Flotation Processes," John Wiley and Sons, New York, p. 41.

[8] O. A. Pickett, in a private communication, Hercules Powder Company, Experimental Station, Kenvil, New Jersey.

[9] A. Schorger, "The Oils of the Coniferae; The Leaf and Twig Oils of Long Leaf Pine and Cone Oils of Long Leaf Pine," *J. Ind. Eng. Chem.*, **6**, 723 (1914).

[10] R. H. Stevens, *Chem. Met. Eng.*, **26**, 37 (1922).

The pinene, dipentene and terpinolene were purified by drying and by from five to eight distillations in a still with a 23-cm. fractionating column.

The physical constants obtained are listed in the table.

| Substance | Density $d_4^{25}$ | $n_D^{25}$ | $(\alpha_s)_D^{25}$ | Boiling point, °C. |
|---|---|---|---|---|
| Pinene | 0.85353 | 1.4671 | +0.83 | 156.1–157.6 |
| Dipentene | .84108 | 1.4748 | +4.38 | 176.3–177.2 |
| Terpinolene | .85768 | 1.4823′ | +0.20 | 185–186.7 |

The symbols have their usual significance; that is, $n_D^{25}$ is the index of refraction at 25° and $(\alpha_s)_D^{25}$ the angle of specific rotation at 25°. Sodium light was used in both measurements.

Borneol was dissolved in a little hot ethyl alcohol and filtered, and then water was added. Then the borneol was removed and the process repeated. The crystals were dissolved in benzene at 70° and were recrystallized when cooled to twenty degrees. They were again filtered, and dried in a vacuum desiccator. The melting point was 207.0–207.5°. It was taken with a sealed tube, since borneol boils at 212°.

α-Terpineol has a decided tendency to supercool when in the liquid state. In a low freezing mixture, however, it crystallizes fairly rapidly. The crystals thus produced were filtered off, dissolved in a small amount of warm alcohol, refiltered and again placed in the freezing mixture. The resulting crystals were dried. The crystals melted at 35° over a one-degree range.

The fenchyl alcohol was similarly treated. Its melting point was 37.8–38.3°.

The camphor was a U. S. P. grade, and no further purification was attempted. It melted at 179.9–180.8°.

The results of the surface and interfacial tension measurements are given in the tables.

TABLE I

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF YARMOUR STEAM DISTILLED PINE OIL AT 25°. MEASURED WITH A HARKINS DROP-WEIGHT APPARATUS

| Concn., g. per 1000 g. of $H_2O$ | Wt. of 1 drop, g. a | b | Surface tension $\gamma_a$ | $\gamma_b$ | $\gamma_{av.}$ |
|---|---|---|---|---|---|
| 0.000 | 0.11034 | 0.11034 | 72.13 | 72.13 | 72.13 |
| .00353 | .11040 | .11039 | 72.16 | 72.13 | 72.14 |
| .00911 | .11034 | .11031 | 72.13 | 72.12 | 72.13 |
| .01265 | .11005 | .11015 | 71.92 | 71.98 | 71.95 |
| .02083 | .10977 | .10977 | 71.93 | 71.79 | 71.85 |
| .03795 | .10836 | .10850 | 70.82 | 70.91 | 70.86 |
| .07495 | .10593 | .10603 | 69.25 | 69.31 | 69.28 |
| .11458 | .10118 | .10109 | 66.14 | 66.08 | 66.11 |
| .15359 | .10036 | .10070 | 65.71 | 65.83 | 65.77 |
| .20313 | .09614 | .09594 | 62.79 | 72.72 | 62.75 |
| .39982 | .08919 | .08913 | 58.26 | 58.27 | 58.26 |
| .86327 | .07822 | .07816 | 50.91 | 50.87 | 50.89 |

The tip radius of the drop-weight apparatus is 0.3985 cm.

The density of the most concentrated aqueous solution of pine oil used was found to be $d_4^{25}$ 0.99696, while that of pure distilled water at this temperature is $d_4^{25}$ 0.99797.

The amount in solution at the highest concentration given was taken as the weight of pine oil added. At this point two distinct phases were visible.

The foregoing data are plotted in Fig. 1.

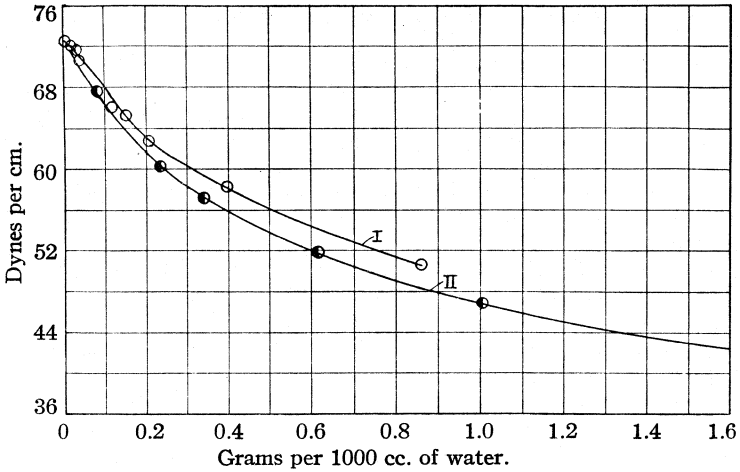


Fig. 1.—Surface tensions of aqueous solutions of pine oil (I) and α-terpineol (II) at 25° given for purposes of comparison.

TABLE II

THE SURFACE TENSIONS OF SATURATED AQUEOUS SOLUTIONS OF CERTAIN TERPENES AT 25°, MEASURED WITH A HARKINS DROP-WEIGHT APPARATUS

| Terpene | Wt. of 1 drop, g. a | b | Surface tension $\gamma_a$ | $\gamma_b$ | $\gamma_{av.}$ |
|---|---|---|---|---|---|
| Pinene | 0.11004 | 0.11009 | 71.91 | 71.93 | 71.92 |
| Dipentene | .10941 | .10937 | 71.53 | 71.48 | 71.51 |
| Terpineolene | .10956 | .10959 | 71.62 | 71.63 | 71.62 |

These terpenes are nearly insoluble in water.

TABLE III

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF CAMPHOR AT 25°

| Molality | Wt. of 1 drop, g. a | b | Surface tension $\gamma_a$ | $\gamma_b$ | $\gamma_{av.}$ |
|---|---|---|---|---|---|
| 0.000000 | 0.11034 | 0.11039 | 72.12 | 72.14 | 72.13 |
| .001009 | .10309 | .10321 | 67.40 | 67.47 | 67.43 |
| .001540 | .10009 | .00984 | 65.42 | 65.27 | 65.34 |
| .005083 | .08759 | .08758 | 57.22 | 57.21 | 57.21 |
| .007250 | .08297 | .08285 | 54.11 | 54.03 | 54.07 |
| .012 | .08002 | .08005 | 52.09 | 52.11 | 52.10 |

The density of the concd. solution is $d_4^{25}$ 0.99699. The tip radius is 0.3985 cm.

The solubility of the saturated solution was taken from the work of Leo and Rimbach.[11]

The solubility of the saturated solution was determined by extrapolation of the surface tension–concentration curve. The density of the concd. solution was $d_4^{25}$ 0.99701.

[11] Leo and Rimbach, *Biochem. Z.*, **950**, 306 (1919).

TABLE IV

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF FENCHYL ALCOHOL

| Molality | Wt. of 1 drop, g. a | b | Surface tension $\gamma_a$ | $\gamma_b$ | $\gamma_{av.}$ |
|---|---|---|---|---|---|
| 0.00000 | 0.11034 | 0.11039 | 72.12 | 72.14 | 72.13 |
| .0003061 | .10612 | .10622 | 69.50 | 69.37 | 69.43 |
| .0006631 | .10045 | .10052 | 65.66 | 65.71 | 65.68 |
| .0013856 | .09820 | .09279 | 60.64 | 60.64 | 60.64 |
| .0021076 | .08829 | .08804 | 57.53 | 57.68 | 67.60 |
| .0024146 | .08639 | .08632 | 56.39 | 56.44 | 56.42 |
| .0034289 | .08240 | .08239 | 53.72 | 53.72 | 53.72 |
| .0040092 | .07992 | .07979 | 52.05 | 51.97 | 52.01 |
| .0067747 | .07404 | .07409 | 48.05 | 48.12 | 48.07 |
| .0078624 | .07178 | .07161 | 46.52 | 46.42 | 46.47 |
| .00840 | .07115 | .07112 | 46.09 | 46.07 | 46.08 |

The tip radius is 0.3985 cm.

TABLE V

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS IN BORNEOL

| Molality | Weight of 1 drop, g. a | b | Surface tension $\gamma_a$ | $\gamma_b$ | $\gamma_{av.}$ |
|---|---|---|---|---|---|
| 0.00000 | 0.11034 | 0.11039 | 72.12 | 72.14 | 72.13 |
| .0000984 | .11001 | .10994 | 71.89 | 71.84 | 71.86 |
| .0003244 | .10705 | .10691 | 69.98 | 69.89 | 69.93 |
| .0006354 | .09954 | .09956 | 65.07 | 65.08 | 65.07 |
| .0009543 | .09510 | .09526 | 62.21 | 62.26 | 62.23 |
| .0012120 | .09326 | .09326 | 60.91 | 60.78 | 60.84 |
| .0019256 | .08694 | .08680 | 56 79 | 56.74 | 56.76 |
| .0031404 | .08051 | .08041 | 52.45 | 52.39 | 52.42 |
| .00407 | .07560 | .07566 | 49.14 | 49.20 | 49.17 |

The density of the concd. solution was $d_4^{25}$ 0.99702. The tip radius is 0.3985 cm.

The solubility of the saturated solution was taken from the work of S. Mitchell.[12]

TABLE VI

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF α-TERPINEOL

| Concn., g. per 1000 g. of $H_2O$ | Molality | Wt. of 1 drop, g. a | b | Surface tension $\gamma_a$ | $\gamma_b$ | $\gamma_{av.}$ |
|---|---|---|---|---|---|---|
| 0.00000 | 0.00000 | 0.11034 | 0.11039 | 72.12 | 72.14 | 72.13 |
| .08088 | .0002245 | .10345 | .10345 | 67.63 | 67.63 | 67.63 |
| .23118 | .001500 | .09212 | .09200 | 60.19 | 60.12 | 60.15 |
| .34200 | .002218 | .08736 | .08741 | 57.07 | 57.10 | 57.08 |
| .61610 | .003995 | .07955 | .07973 | 51.92 | 51.81 | 51.86 |
| 1.0331 | .006704 | .07250 | .07247 | 47.01 | 47.03 | 47.02 |
| 1.71102 | .011095 | .06598 | .06590 | 41.79 | 41.84 | 31.82 |
| 2.10 | .0136 | .06004 | .05997 | 38.39 | 38.36 | 38.38 |

The tip radius is 0.3985 cm. The density of concd. soln. is $d_4^{25}$ 0.99691.

Concentrated solution surface tension was redetermined with another tip. The results were as follows:

[12] S. Mitchell, THIS JOURNAL, **48**, 1333 (1926).

| G. per 1000 g. of $H_2O$ | Molality | Wt. of 1 drop, g. | | Surface tension $\gamma_a$ | $\gamma_b$ | $\gamma_{av.}$ |
|---|---|---|---|---|---|---|
| 2.10 | 0.0136 | 0.06004 | 0.05997 | 38.56 | 38.50 | 38.53 |

The tip radius was 0.2702 cm.

The solubility found by Rhode[13] was 1.98 g. or 0.0129 mole per liter at 15–20° for terpineol in aqueous solution.

The concentration given for the saturated solution is slightly larger. It was determined by extrapolation of the surface tension–concentration curve for the data given above.

The data for the terpene alcohols and camphor are plotted in Fig. 2.

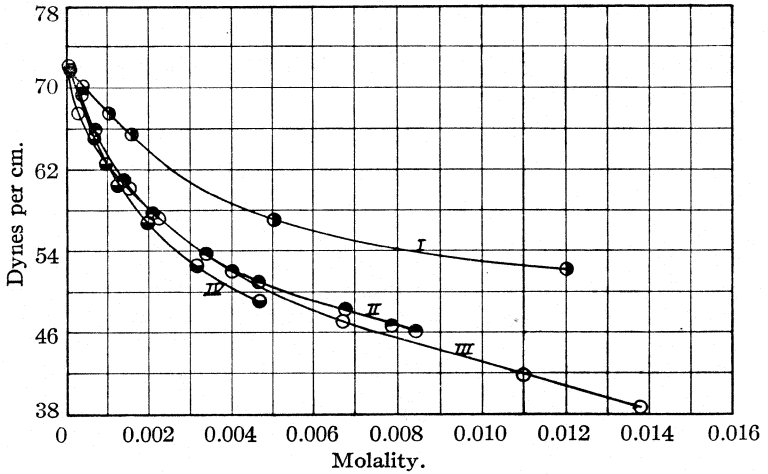


Fig. 2.—Surface tensions of aqueous solutions of (I), camphor, (II), fenchyl alcohol, (III), α-terpineol and (IV), borneol at 25°.

TABLE VII

THE SURFACE TENSION RELATIONSHIPS OF AQUEOUS SOLUTIONS OF α-TERPINEOL AND DIPENTENE

| | G. of dipentene per 1000 cc. of $H_2O$ | G. of α-terpineol per 1000 cc. of $H_2O$ | Surface tension $\gamma$ |
|---|---|---|---|
| (1) | 0.36848 | 1.44184 | 52 01 |
| (2) | .36848 | 0.00000 | 71.50 |
| (3) | .00000 | 1.44184 | 44.10 |
| (4) | .75306 | 0.89406 | 54.21 |
| (5) | .00000 | .89406 | 49.15 |
| (6) | .75306 | .00000 | 71.50 |

Data for grams of α-terpineol per 1000 cc. of water shown in the horizontal columns (3) and (5) were taken from the surface tension concentration diagrams for aqueous solutions of α-terpineol. Data for grams of dipentene per 1000 cc. of water shown in horizontal columns (2) and (6) were taken from the result for the saturated solution since the solubility is

[13] Rhode, *Biochem. Z.*, **130**, 481–496 (1922).

considerably less than the amounts of dipentene used. Data in horizontal columns (1) and (4) were measured directly and the surface tensions given are the average of two determinations.

TABLE VIII

THE INTERFACAL TENSION BETWEEN PINENE AND AQUEOUS SOLUTIONS OF α-TERPINEOL

| Mole of terpineol solution | Vol. of drops, ml. | Interfacial tension, dynes/cm. |
|---|---|---|
| 0.00000 | 0.5737 | 26.69 |
| .001500 | .5717 | 26.67 |
| .003995 | .5700 | 26.50 |
| .006705 | .5710 | 26.65 |
| .01360 | .5716 | 26.58 |

The density of the pinene was $d_4^{25}$ 0.85353. The tip radius is 0.7969. The density of the satd. terpineol sol. was $d_4^{25}$ 0.99699.

TABLE IX

THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF POTASSIUM ETHYL XANTHATE

| Molality | Wt. of 1 drop, g. a | b | $d_4^{25}$ | Surface tension $\gamma_a$ | $\gamma_b$ | $\gamma_{av.}$ |
|---|---|---|---|---|---|---|
| 0.00000 | 0.11034 | 0.11039 | 0.99707 | 72.12 | 72.14 | 72.13 |
| .08392 | .10965 | .10954 | 1.0025 | 71.66 | 71.59 | 71.62 |
| .32480 | .10858 | .10860 | 1.0146 | 70.82 | 70.83 | 70.82 |
| .63774 | .10599 | .10597 | 1.0365 | 69.26 | 69.28 | 69.27 |
| .66189 | .10618 | .10594 | 1.0382 | 69.39 | 69.24 | 69.31 |
| .92137 | .10429 | .10430 | 1.0507 | 68.18 | 68.18 | 68.18 |
| 1.0418 | .10341 | .10319 | 1.0562 | 67.59 | 67.46 | 67.52 |
| 1.2898 | .10146 | .10166 | 1.0670 | 66.31 | 66.44 | 66.37 |
| 2.1815 | .09770 | .09761 | 1.1104 | 63.70 | 63.64 | 63.67 |
| 5.2559 | .08920 | .08801 | 1.1994 | 57.29 | 57.17 | 57.23 |
| 6.70 | .08514 | .08509 | 1.2256 | 55.08 | 55.06 | 55.07 |

The tip radius is 0.3985 cm.

The foregoing data are plotted in Fig. 3. The molality of the saturated solution was determined by extrapolation of a density–concentration curve (not shown).

## Discussion of Results

The results obtained by DeWitt and Roper[2] through the use of the Ferguson–Dowson method for the measurement of the surface tension of aqueous solutions of potassium ethyl xanthate are in close agreement with those obtained by the drop-weight method in this Laboratory. Therefore, in the measurement of the surface tensions of aqueous solutions of potassium ethyl xanthate by the Ferguson–Dowson method, there is good reason for assuming that the contact angle is zero or, at least, that it is negligible.

The results obtained for the surface tensions of aqueous pine oil solutions are in accord with those which Fahrenwald[14] secured by the drop-weight

[14] A. W. Fahrenwald, *Trans. Am. Inst. Met. Min. Eng.*, **70**, 647 (1924).

method, but do not agree with those which he obtained with the Jaeger and Fahrenwald methods.

The compounds pinene, dipentene and terpinolene have but little effect on the surface tension of water. Taggart and Guadin[15] found that very slightly soluble substances are not good frothers.

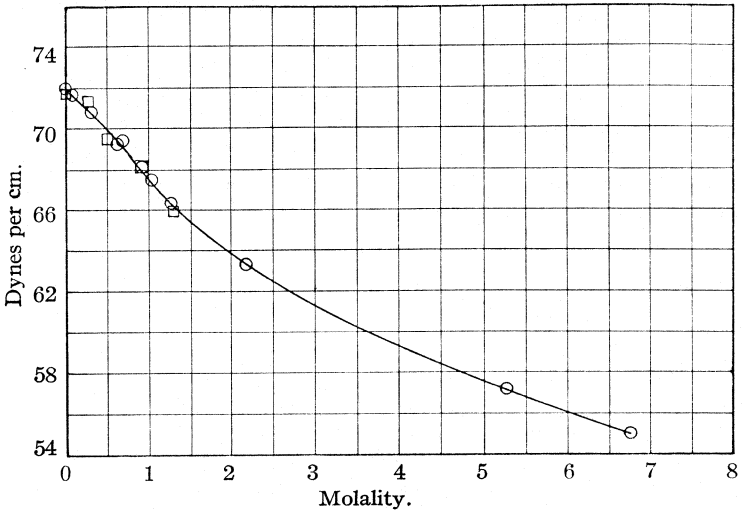


Fig. 3.—The surface tensions of aqueous solutions of potassium ethyl xanthate at 25°. The concentration of the last point was determined by extrapolation of density–concn. curve. Squares represent points determined by DeWitt and Roper using the Ferguson–Dowson method. The circles represent determinations made by the drop-weight method.

Harkins and Cheng[16] state that the highly polar group is necessary to adsorption at the liquid interface. They found that the adhesional energy is greatly increased by the addition of oxygen but is little affected by the presence of the double bond. Since terpineolene, pinene and dipentene all have double bonds but no oxygen, little effect on the surface tension of the water solution would be expected. In spite of the slight effect of these compounds, they appear to act as froth stabilizers by increasing the viscosity of the surface film.[17]

The introduction of the hydroxyl group either into the monocyclic ring, as in fenchyl alcohol or borneol, or in the side chain as in α-terpineol, greatly increases the solubility and surface tension lowering effect. An inspection of the surface tension–concentration curves shows that lowering of surface tension of a dilute aqueous solution is practically the same regardless of the position of the OH radical for the terpene alcohols studied. The effective-

[15] Taggart and Guadin, *Trans. Am. Inst. Met. Min. Eng.*, **68**, 479 (1923).

[16] Harkins and Cheng, THIS JOURNAL, **43**, 35 (1921).

[17] Wilson, "Colloid Chemistry," Alexander, Ref. 6, p. 276

ness, per mole, of camphor is slightly more than half that of borneol and is probably due to the substitution of the O for the OH in the otherwise similar compounds. There is some relation between the position of the hydroxyl group and the solubility, a relation which affects the lowering of surface tension in concentrated solutions.

The work reported here would indicate that terpineol, borneol and fenchyl alcohol are nearly equally effective as frothing agents at the concentrations used in flotation practice. However, according to O. A. Pickett[8] $\alpha$-terpineol constitutes 40% or more of Yarmour pine oil. The fenchyl alcohol constitutes about 8%, and the borneol 10%.

The presence of dipentene, and presumably of the other terpenes, greatly decreases the effectiveness of $\alpha$-terpineol as a surface tension lowering agent in water solution. At the concentration at which measurements were made, roughly half the weight of terpineol would have achieved the same surface tension lowering had no dipentene been present.

Further evidence of the loss in effectiveness of the $\alpha$-terpineol is shown by a comparison of the surface tension–concentration curves of aqueous solutions of pine oil and $\alpha$-terpineol. The terpineol curve is steeper.

Guadin, Glover, Hansen and Orr[18] have measured the surface tensions of terpineol solutions by the du Nouy method. Their results are not in agreement with the results obtained in this Laboratory. The discrepancy in values is probably due to the difference in results found by Harkins, Young and Cheng,[19] who compared the du Nouy and drop-weight methods.

The interfacial tension of aqueous solutions of $\alpha$-terpineol against pinene did not change with concentration. Since the $\alpha$-terpineol is very soluble in pinene, however, most of it is probably in the pinene phase. The interfacial tension of pinene–aqueous solutions of $\alpha$-terpineol is high, a fact which indicates very little mutual attraction of the water and pinene molecules.

## Summary

1. The surface tension–concentration curves of potassium ethyl xanthate have been extended. Good agreement has been found to exist between the measurements given by the drop-weight method and those obtained by Roper and DeWitt through the use of the Ferguson–Dowson method.

2. The addition of the compounds $\alpha$-pinene, terpinolene, and dipentene affects but slightly the surface tensions of the water solutions.

3. The lowering of surface tension in dilute aqueous solutions of the terpene alcohols, borneol, $\alpha$-terpineol, and fenchyl alcohol is nearly the same. The variation becomes greater in concentrated solutions, since not all are of the same solubility.

[18] Guadin, Glover, Hansen and Orr, University of Utah Technical Paper No. 1, p. 7

[19] Harkins, Young and Cheng, *Science*, 64, 333 (1926).

4. The surface tensions of aqueous camphor solutions change much less rapidly with concentration than do those of the aqueous solutions of borneol.

5. The presence of the dipentene and presumably of the other terpenes lowers the effectiveness of $\alpha$-terpineol as a frothing agent in so far as that property can be determined by surface and interfacial tension methods.

HOUGHTON, MICHIGAN

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF VICTOR CHEMICAL WORKS]

# THE CATALYTIC EFFECT OF ALKALI AND ALKALINE EARTH SULFIDES ON THE REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR

BY WILLARD H. WOODSTOCK AND HOWARD ADLER

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In connection with work in this Laboratory on the preparation of phosphorus thiochloride, the reaction between phosphorus trichloride and sulfur as first reported by L. Henry[1] was investigated. A repetition of his experiment disclosed almost complete absence of reaction at 150° at the end of two hours and only partial reaction after eight hours' time.

Since such a reaction afforded a direct as well as simple means of preparing phosphorus thiochloride, it was hoped that further investigation would reveal a method of obtaining more complete reaction in shorter experimental periods.

## Experimental

**Sulfur.**—C. P. flowers of sulfur were used.

**Phosphorus Trichloride.**—The phosphorus trichloride was made by the direct combination of yellow phosphorus and dry chlorine gas. The crude product was redistilled over fresh yellow phosphorus to remove any pentachloride. The boiling point of the final product was 76°.

**Sodium Polysulfide.**—Technical sodium monosulfide, $Na_2S \cdot 9H_2O$, was dehydrated by fusion. By heating together calculated quantities of anhydrous sodium monosulfide and sulfur, anhydrous sodium polysulfide was obtained. It was stored in a desiccator.

**Other Sulfides.**—The potassium, calcium and barium sulfides were of technical grade. They were dried before using.

**Procedure.**—The experiments at atmospheric pressure were carried out in an all-glass refluxing apparatus. The theoretical quantities of the reactants were placed in a 250-cc. round-bottomed flask attached to a reflux condenser by a ground-glass joint. At the top of the condenser was mounted a drying tube of phosphorus pentoxide to prevent moisture from entering the apparatus. At the end of the experiment the liquid in the flask was distilled from any residue into a distilling flask preparatory to determining its boiling range and gravimetric analysis.

When experimenting at elevated temperatures, sealed Pyrex tubes were used. The

[1] L. Henry, *Ber.*, **2**, 638 (1869).

period of heating was controlled by placing the sealed tubes in preheated iron sheaths which were removed from the oven and quenched in cold water after the desired length of time.

Larger quantities of materials under pressure were handled in an oil-jacketed, steel autoclave which was equipped with a motor-driven agitator, extra-heavy pipe fittings, needle-valves and a pressure gage. Although iron was used throughout its construction, no signs of corrosion were evident after several runs. The product was distilled directly from the autoclave and redistilled in glass.

## Results

The effects of time, temperature and catalysts on the condensation of phosphorus trichloride and sulfur were studied. It was felt that if the sulfur were present in a more reactive form, such as an anhydrous alkali or alkaline earth polysulfide, the yield of phosphorus thiochloride would be increased. The equation for such a reaction may be written

$$4PCl_3 + Na_2S_5 = 4PSCl_3 + Na_2S$$

This possibility as a solution to the problem was studied in conjunction with the direct reaction with sulfur.

In Table I are given the results of the experiments conducted at atmospheric pressure and at the boiling point of phosphorus trichloride.

TABLE I

REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR AT THE BOILING POINT OF THE SOLUTION

| Experiment | $PCl_3$, g. | S, g. | $Na_2S_5$, g. | Time, hours | Boiling range of product, °C. |
|---|---|---|---|---|---|
| 1 | 100 | 23.3 | None | 12 | 74– 79 |
| 2 | 100 | 23.3 | None | 24 | 74– 81 |
| 3 | 53.8 | None | 20.2 | 11 | 74– 85 |
| 4 | 120 | None | 45.0 | 24 | 105–122 |
| 5 | 39.4 | 9.2 | 0.5 | 11 | 74– 78 |

No reaction occurred when the two reactants were refluxed together for a reasonable length of time. When the calculated amount of sulfur was added in the form of anhydrous sodium polysulfide, $Na_2S_5$, a slow reaction took place as evidenced in Experiments 3 and 4. However, when a relatively small amount of the polysulfide was added to the phosphorus trichloride–sulfur mixture in an attempt to catalyze the direct reaction, the results were negative.

When higher temperatures were tried, namely 150°, an increase in the yield of phosphorus thiochloride was immediately apparent. In Table II, Experiments 6, 7 and 8 show the effect of time upon the reaction, which was still incomplete at eight hours. The next two experiments indicate that complete reaction may be obtained with the substitution of sodium polysulfide for the sulfur, while in Experiment 11 the presence of a small amount of polysulfide materially increased the rate of reaction between sulfur and phosphorus trichloride.

TABLE II

REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR AT 150°

| Experiment | $PCl_3$, g. | S, g. | $Na_2S_5$, g. | Time, hours | Boiling range of product, °C. |
|---|---|---|---|---|---|
| 6 | 39.4 | 9.2 | None | 2 | 74– 78 |
| 7 | 39.4 | 9.2 | None | 4 | 75– 90 |
| 8 | 39.4 | 9.2 | None | 8 | 85–122 |
| 9 | 39.4 | None | 14.8 | 4 | 120–125 |
| 10 | 78.8 | None | 29.6 | 1 | 119–126 |
| 11 | 39.4 | 9.2 | 0.5 | 4 | 110–124 |

As a result of the above experiments, it appeared feasible to prepare phosphorus thiochloride from phosphorus trichloride and sodium polysulfide. It seemed more desirable, however, to develop the reaction between phosphorus trichloride and sulfur with the aid of the catalytic influence of small amounts of sodium sulfide. In continuing the investigation, the latter reaction was carried out on a slightly larger scale in a steel experimental autoclave. Sulfides of the other alkali and alkaline earth metals, namely, potassium, calcium and barium sulfides, were also tested for their effect upon the reaction.

The results of the experiments are presented in Table III. Experiments 12 and 13 were run as blanks with no catalyst present. They confirmed the slowness of reaction obtained in the experiments with sealed tubes. All the sulfides tried were effective catalysts. The alkaline earth sulfides appeared to have weaker catalytic activity than the alkali sulfides.

TABLE III

REACTION BETWEEN PHOSPHORUS TRICHLORIDE AND SULFUR AT 150–160°

Charges consisted of 315 g. of phosphorus trichloride, 74 g. of sulfur and 3.9 g. (1%) of catalyst.

| Experiment | Catalyst | Time, hours | Boiling range of product, °C. |
|---|---|---|---|
| 12 | None | 4 | 78– 85 |
| 13 | None | 8 | 80–123 |
| 14 | $Na_2S$ | 5 | 118–124 |
| 15 | $Na_2S$ | 2 | 119–124 |
| 16 | $K_2S$ | 4 | 119–124 |
| 17 | CaS | 4 | 102–123 |
| 18 | BaS | 4 | 107–123 |

The boiling point of phosphorus trichloride is 76°, while that of phosphorus thiochloride is 123° at the barometric pressure under which the experiments were made. The boiling points were considered far enough apart to be used in judging the general extent of reaction. The thermometer readings given in the tables above are uncorrected.

In order to gain a more exact knowledge of the extent of reaction, gravimetric analyses of several of the products were made by the Carius method. The results are given in Table IV.

TABLE IV

ANALYSIS OF REACTION PRODUCTS

| Experiment | P found, % (Calcd. for $PCl_3$: P, 22.58.) | S found, % (Calcd. for $PSCl_3$: P, 18.31; S. 18.88) | $PSCl_3$ (from S), % |
|---|---|---|---|
| 6 | 22.47 | 0.61 | 3.23 |
| 7 | 21.19 | 6.19 | 32.74 |
| 8 | 19.81 | 12.68 | 67.16 |
| 9 | 18.53 | 19.14 | 100.0 |
| 14 | 18.69 | 18.29 | 96.87 |
| 15 | 18.62 | 18.72 | 99.15 |

The mechanism of the catalysis may well be explained by the intermediate compound theory in which the polysulfide is the active agent. Thus any basic substance with which sulfur easily reacts to give addition compounds would probably serve as a condensing agent for the reaction. For example, it has been observed that free caustic soda will catalyze the reaction. It was customary to clean the autoclave with hot caustic soda solution after each experimental run, and if the alkali were not thoroughly removed, reaction resulted in those experiments where no catalyst had been added.

## Summary

Phosphorus trichloride and sulfur do not react at atmospheric pressure and at the boiling point of the solution. At 150° a slow, partial reaction to form phosphorus thiochloride takes place.

Small amounts of alkali metal sulfides, alkaline earth metal sulfides or substances of like character which add on sulfur catalyze the reaction between phosphorus trichloride and sulfur so that conversion to phosphorus thiochloride is complete at 150° within a short period of time.

CHICAGO HEIGHTS, ILLINOIS

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

# THE PHOTOCHEMICAL DECOMPOSITION OF ORGANIC ACIDS[1]

BY W. C. PIERCE AND GLEN MOREY

RECEIVED SEPTEMBER 1, 1931 PUBLISHED FEBRUARY 5, 1932

Quantitative studies have been made of the photochemical decomposition of aqueous solutions of oxalic,[2] formic,[3] lactic[4] and malonic[5] acids. Oxalic acid absorbs light of wave lengths below 365 mμ, decomposing to formic acid and carbon dioxide. The quantum yield is small. Formic acid de-

[1] A report of part of this work was presented at the Fall Meeting of the American Chemical Society at Minneapolis, 1929.

[2] Allmand and Reeve, *J. Chem. Soc.*, **129**, 2834 (1926).

[3] Allmand and Reeve, *ibid.*, **129**, 2852 (1926).

[4] Burns, THIS JOURNAL, **51**, 3165 (1929).

[5] Pierce, Leviton and Noyes, *ibid.*, **51**, 80 (1929).

composes in two ways, giving either carbon dioxide and hydrogen or carbon monoxide and water. The quantum yield is near unity for light of wave length near 300 mμ and rises for light of shorter wave length. Lactic acid gives carbon dioxide as the chief gaseous product. The quantum efficiency is about 0.65 in dilute solution. According to previous work in this Laboratory[5] malonic acid absorbs light in the ultraviolet region, decomposing to give carbon dioxide and acetic acid. The quantum efficiency was estimated as 0.75 ± 0.25 for 0.05 *m* solutions. The decomposition was thought to be due to undissociated molecules since addition of strong acids did not affect the light sensitivity. The reaction, like that of oxalic acid, is sensitized to light of longer wave lengths by the addition of uranyl salts, but the quantum efficiency of the sensitized reaction is less than for the unsensitized.

In the present work a more thorough study of the mechanism of the photochemical decomposition of organic acids is undertaken. Because of the simplicity of its decomposition malonic acid was first investigated.

**Change in Rate with Concentration.**—Duplicate samples of varying concentration were lighted simultaneously on a rotating stand in order to insure uniformity of illumination. The full light of a vacuum type mercury arc lamp was used. The amount of decomposition was determined by titration with sodium hydroxide, unlighted samples being used as controls for each determination. The experimental error was large since the total decomposition had to be kept low in order to prevent complete decomposition of the more dilute samples. A summary of the results is given in Table I. The average concentration was taken as the arithmetical mean of the initial and final concentrations. The variation in rate is much less than the variation in concentration, but it is possible that this is due to decomposition of acetic acid in the more dilute samples, thus making the apparent rate larger than the true value.

TABLE I

VARIATION IN RATE WITH CONCENTRATION

| Run | Initial concn., *m* | Decompn., cc. NaOH | Per cent. decompn. | Av. ratio concn. | Ratio of rates |
|---|---|---|---|---|---|
| 1 | 0.1 | 4.65 | 22 | | |
| | .01 | 1.27 | 64 | 13 | 3.7 |
| 2 | .1 | 1.92 | 9 | | |
| | .01 | 0.54 | 39 | 12 | 3.6 |
| 3 | .1 | 2.43 | 11 | | |
| | .01 | 0.97 | 58 | 13 | 2.5 |

**Variation in Absorption with Concentration.**—It was thought that the small variation in rate shown in Table I might be due to variation in the amount of light absorbed by the solutions. In order to test this the total absorption of light was determined for the concentrations used in the

experiments. A parallel beam of light was passed through a layer of solution and the intensity measured by a sensitive thermopile. Blank determinations were made with the solution replaced by a vessel filled with distilled water. The fraction of the total light absorbed by solutions of various concentration is shown in Fig. 1. At small concentrations the fraction of the light absorbed seems to vary as the concentration. Because of the inherent large errors in this and the preceding experiment no conclusions may be safely drawn as to the order of the reaction except that it is not higher than first order.

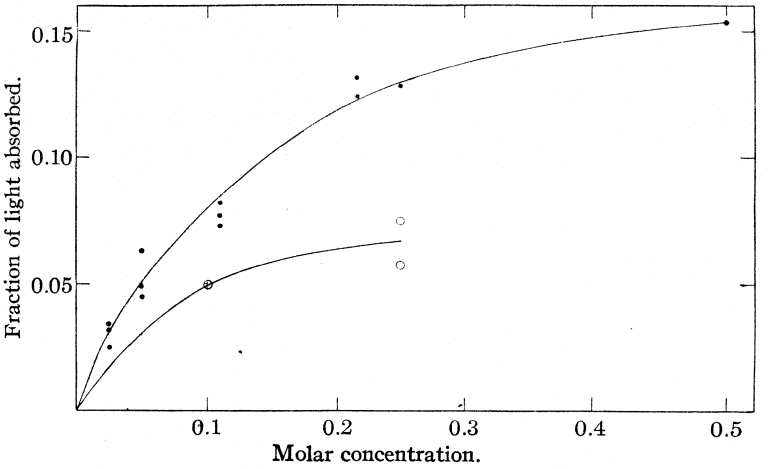


Fig. 1.—Fraction of light from mercury arc lamp absorbed by malonic acid (upper) and sodium malonate solutions.

**Effect of Salt Formation.**—A comparison was made of the relative rates of decomposition of malonic acid and sodium malonate, 0.1 *m* samples of each being lighted simultaneously. Hydrolysis of the salt solution was prevented by the addition of a slight excess of sodium hydroxide. The amount of decomposition of the salt solution was determined by adding excess sulfuric acid, boiling off the evolved carbon dioxide and titrating the remaining acid with standard sodium hydroxide. An unlighted sample was used as a control test in each experiment. The procedure was based on the following reactions

$$Na_2C_3H_2O_4 + H_2O + \text{light} = NaOH + NaC_2H_3O_2 + CO_2$$
$$NaOH + CO_2 = NaHCO_3$$
$$NaHCO_3 + H_2SO_4 = NaHSO_4 + CO_2$$

That this is the course of the reaction was proved by testing for acetate after lighting and by the absence of gas evolution from a lighted sample of the salt solution. The relative rate of decomposition of malonic acid was found to be about five times that of sodium malonate.

**Absorption Spectra.**—The total absorption of sodium malonate solutions was determined for various concentrations. The results are shown in the lower curve of Fig. 1. Since the absorption is about half that of the malonic acid and the rate of decomposition about one-fifth, the quantum efficiency is estimated to be about one-half that of malonic acid.

The molar absorption coefficients[6] of acid and salt were determined by the rotating sector method with a Hilger E2 quartz spectrograph. The values are plotted in Fig. 2 for various wave lengths. In all measurable regions the acid shows a much higher absorption than the salt. The results are in agreement with the measurements of Bielecki and Henri[7] for malonic acid and with the observation of Wright[8] that salt formation lowers the absorption of light.

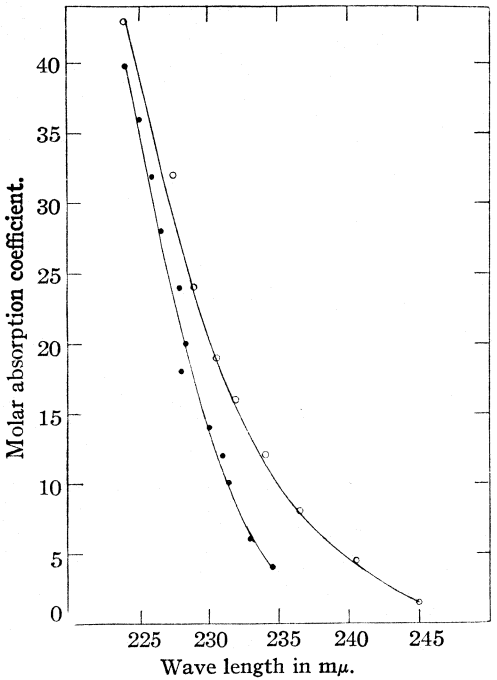


Fig. 2.—Molar absorption coefficients of malonic acid (upper) and sodium malonate.

**Temperature Coefficient.**—The temperature coefficient was determined by simultaneous lighting of two samples, one at 3° and the other at 70°. Two quartz test-tubes, surrounded by quartz water jackets, were mounted in optically equivalent positions near the lamp and the desired temperatures maintained by a rapid flow of water through the jackets. The "ten degree" temperature coefficient was found to be 1.07 for the range investigated. This is not due to a change in absorption, for hot and cold samples were found to absorb the same amount of light.

**Acetic and Propionic Acids.**—Aqueous solutions of these acids were lighted in an enclosed apparatus and the evolved gases pumped off and analyzed. For acetic acid the main products were equivalent quantities of

[6] By "molar absorption coefficient" is meant the constant of the Beer's law equation

$$\log I_0/I = kcd$$

in which $k$ is the constant, $c$ is the molar concentration and $d$ is the thickness in centimeters.

[7] Bielecki and Henri, *Ber.*, **45**, 2819 (1912).

[8] Wright, *J. Chem. Soc.*, **103**, 528 (1913).

carbon dioxide and methane with small quantities of carbon monoxide and unsaturated hydrocarbons. The chief products for propionic acid were carbon dioxide and ethane in equivalent quantities. The hydrocarbons were identified by explosion with oxygen.

## Discussion and Conclusions

The decomposition of malonic acid after activation by light seems to be independent of concentration since the variation in rate with concentration is less than the variation in concentration. The quantum efficiency of the reaction may be recalculated on the basis of the present absorption measurements, giving a value of 0.5 ± 0.25 molecule per quantum for the whole light of the mercury arc lamp. No attempt has been made to employ monochromatic light because of the low intensity of the short wave lines of the mercury spectrum.

Qualitative confirmation of the low quantum efficiency may be obtained from the temperature coefficient. According to Tolman's theory of the temperature coefficient only molecules having an energy content above the average may decompose on absorption of light in reactions having a temperature coefficient larger than unity. Calculations based on the present value of 1.07 for the temperature coefficient indicate that an energy increment of about 600 calories per mole is necessary for the molecules that may decompose. The probability that a molecule will have this amount of excess energy is about 0.4, a value in agreement with the observed quantum efficiency.

The results with sodium malonate show that the decomposition is not due primarily to the ions present, confirming the previous findings with respect to the addition of strong acids. However, it seems that the course of the reaction is the same for the salt and acid since the same products are obtained, namely, carbon dioxide and acetic acid or acetate ion. The results with acetic and propionic acids, when considered with the above, lead to the conclusion that the primary process in the decomposition of organic acids is a splitting out of carbon dioxide, leaving the remainder of the molecule unchanged. No definite reason may be given for the smaller absorption and the decreased quantum efficiency for the salt, although the similarity in the processes suggests that light is absorbed by the O–H valence electrons of the acid and that in the ion these are more tightly held, requiring more energy for activation.

No attempt has been made to determine the quantum efficiency for acetic and propionic acids, but a qualitative comparison of the velocity of decomposition with that of malonic acid shows about the same rates. Since the absorption also lies in the same region, the quantum efficiency is probably of the same order.

For an organic acid showing a low quantum efficiency, such as oxalic,

the absorption is over a much wider region. Allmand and Reeve[3] found quantum efficiencies ranging from 0.01 at 265 mμ to 0.00095 at 365 mμ. Possibly only the light absorbed by the carboxyl group causes decomposition, and apparently this lies in the region below 250 mμ.

## Summary

A further study is made of the photochemical decomposition of malonic acid and the results obtained are applied to the general process of photochemical decomposition of carboxyl groups. The effective light in this process seems to lie in the region 200–250 mμ. Decomposition gives as products carbon dioxide and a hydrocarbon residue. Photochemical decarboxylations are characterized by low temperature coefficient, quantum efficiency near unity, low absorption of light. Presence of other absorbing groups in the molecule may modify these characteristics.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

# GLACIAL ACETIC ACID AS A SOLVENT FOR THE ELECTRODEPOSITION OF METALS.[1,2] AN X-RAY DIFFRACTION STUDY OF THE STRUCTURE OF DEPOSITS OF ARSENIC, ANTIMONY AND BISMUTH

BY C. W. STILLWELL AND L. F. AUDRIETH

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A considerable number of investigations have demonstrated that a variety of solvents may be employed for the electrodeposition of metals,[2c] and in some instances these studies have shown that certain non-aqueous solvents may be employed with distinct advantage over water. A survey of solvents used for this purpose reveals that they are all either basic or amphiprotic in nature and that no definitely acidic solvent has yet been investigated. However, most compounds of such elements as arsenic, antimony, bismuth and stannic tin undergo considerable solvolysis in basic solvents and dissolve only in the presence of acids. The striking solubility of the chlorides of these elements in glacial acetic acid with the apparent non-formation, at least of insoluble, solvo-basic products, indicated immediately that it might be of considerable theoretical interest to study the discharge of these metallic cations from glacial acetic acid.

Glacial acetic acid has been shown to be an excellent ionizing medium

[1] This paper was presented at the Buffalo meeting of the American Chemical Society, September, 1931.

[2] For earlier papers of this series see (a) Yntema and Audrieth, THIS JOURNAL, **52**, 2693 (1930); (b) Audrieth and Yntema, *J. Phys. Chem.*, **34**, 1903 (1930); (c) Audrieth and Nelson, *Chem. Reviews*, **8**, 335 (1931); (d) Audrieth, Jukkola, Meints and Hopkins, THIS JOURNAL, **53**, 1805 (1931).

and, as Davidson[3] has pointed out, may be regarded as the parent solvent of a system of acids, bases and salts. Because of its limited proteolytic activity it has been characterized as a very acidic solvent by Hall.[4]

No attempt has yet been made to determine the effect of change of solvent upon the character of metallic deposits. In their study of the electrodeposition of metals from liquid ammonia at $-33°$ Audrieth and Yntema[2b] regarded it as quite significant that tin was deposited as white tin rather than in the form of gray tin, the modification stable at that temperature. However, Cohen[5] has pointed out that "most metals are electrodeposited in a metastable form," thus making it difficult to obtain suitable metallic plates except under very special conditions.

Cohen and Coffin[6] have recently shown that concentration and temperature are the two factors which most profoundly affect the electrodeposition of antimony from strongly acidified aqueous solutions of the chloride. Changes in current density appear to be only of minor importance. Thus, at low temperatures and high concentrations the metastable or "explosive" modification is always deposited, whereas low concentrations and high temperatures favor the formation of the crystalline or stable form of the metal. These data suggested the advisability of studying the deposition of antimony from glacial acetic acid solutions to determine the effect of change of solvent. Cohen and Coffin used the appearance of the deposits as the basis for their conclusions, whereas the data given by the authors were determined by an x-ray diffraction study of the deposited metals.

## Experimental[7]

**Electrodeposition of Antimony from Glacial Acetic Acid.**—Antimony can be deposited from glacial acetic acid solutions of the chloride over a wide range of experimental conditions at room temperatures. The concentrations of solutions were varied from 5 to 55 g. of antimony trichloride per 100 g. of solution, the current densities from 0.001 to 0.04 ampere per square centimeter. All experiments were carried out using a 110-volt direct current in series with a lamp-bank for variable resistance. The electrolytic cell was immersed in a constant temperature bath and fitted with a stirrer to prevent local impoverishment of antimony ions in the

[3] Davidson, *Chem. Reviews*, **8**, 175 (1931).

[4] Hall, *ibid.*, **8**, 191 (1931).

[5] Cohen, "Physico-chemical Metamorphosis and Problems in Piezochemistry," Vol. I, George Fisher Baker Non-resident Lectureship Series, McGraw-Hill Book Co., Inc., New York, **1926**, p. 44.

[6] Cohen and Coffin, *Z. physik. Chem.*, Abt. [A] **149**, 417 (1930).

[7] The authors wish to take this opportunity to acknowledge their indebtedness to Mr. Harlan W. Nelson and to Mr. Lionel H. Smith, who performed some of the preliminary experimental work involving the electrodeposition of metals from glacial acetic acid.

neighborhood of the cathode. Two anodes of pure antimony were used between which was placed the cathode.

Deposits of antimony at room temperatures are smooth and possess a black metallic luster. While fairly adherent at first, all of these plates tend in time to dust off and to become non-adherent. Solution of the original metal deposits in nitric acid and subsequent analysis showed that in all cases a considerable amount of antimony trichloride had been adsorbed, indicating that possibly the "explosive" or metastable form had been deposited. This supposition was subsequently verified, first, by comparing the deposits obtained from acetic acid with those obtained from acidified aqueous solutions of the chloride under conditions known to give the metastable modification,[8] proving their macroscopic identity; second, by immersing thicker deposits in an oil-bath and heating slowly to 100°, at which temperature violent disruption of the antimony plates usually occurred.[8]

Attempts to discharge antimony at higher temperatures invariably resulted in the formation of black, pulverulent deposits. In general, deposits upon brass and copper were found to be more adherent than those upon platinum. The addition of water to the electrolytic bath, while not affecting the type of deposit, was found to lower very appreciably the resistivity of the solutions.

The effect of concentration and temperature on the structure of the deposits was investigated systematically for concentrations varying from 7.5 g. to 40 g. of antimony trichloride in 100 g. of solution, and temperatures varying from 20 to 65°. It was found that current density could be varied between 0.01 and 0.07 ampere per square centimeter without affecting the nature of the deposit. Consequently, no attempt was made to keep the current density absolutely constant. For all the data recorded in Fig. 1, however, the current density was kept at 0.03 ± 0.01 ampere per square centimeter. The antimony was deposited on copper, and the results given in Fig. 1 are therefore not strictly comparable with those of Cohen and Coffin,[6] who used platinum as the base metal.[9]

The structure of the deposits was established by x-ray diffraction patterns. These offer more conclusive evidence than the tests described above, which were doubtful for many of the specimens examined. It has recently been shown that explosive antimony is amorphous,[8] and when it explodes it changes to the usual rhombohedral form. There should be little difficulty in distinguishing the two forms by a mere inspection of their diffraction patterns.

[8] Steinwehr and Schulze, *Z. Physik*, **63**, 815 (1930).

[9] It was found difficult to obtain consistent results when platinum was used as the base metal. The reason for this is as yet unknown, although it is the authors' experience that antimony deposited from glacial acetic acid solution never adheres as well to platinum as it does to copper.

Powder patterns were obtained, using the General Electric Multiple Diffraction apparatus with Mo $K_\alpha$ radiation. The antimony was deposited on a 22-gage copper wire which was set in the regular specimen holder of the quadrant cassette, the diffraction pattern being produced by the reflection of x-rays from the surface of the specimen. It is essential, of course, that the diffraction pattern be obtained without disturbing the deposit. In all the cases the deposit was so thin that the pattern for copper was always present on the film. The time of exposure varied from twenty-four to forty-eight hours at 20 ma.

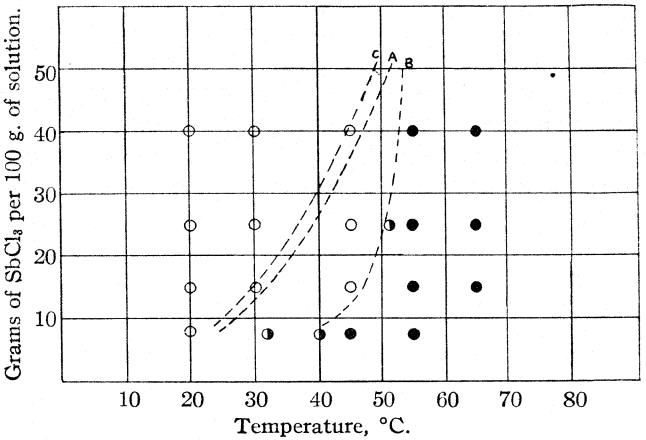


Fig. 1.—○, Amorphous; ●, crystalline; ◑, mixtures.

The diffraction pattern of the crystalline deposits was identified by direct comparison with the diffraction pattern for pure crystalline antimony. The absence of any lines other than those of copper indicates the presence of the explosive form, provided the following two sources of error have been considered. If a crystalline deposit is too thin, it will not give any diffraction pattern. This source of error was eliminated by heating all of the apparently amorphous deposits above the transition temperature to effect their change to the crystalline state. If a crystalline diffraction pattern is then obtained it indicates the sufficient thickness of the deposit and shows that the original deposit was amorphous.

It is well known that in an electrodeposited film the crystal grains usually exhibit preferred orientation with respect to the base metal. Such a condition might lead to an erroneous interpretation of the diffraction pattern, since it might happen that very few, if any, of the planes would reflect in the proper direction to be caught on the photographic plate. Bismuth films, reported in an earlier work to be amorphous, have recently been shown to be crystalline, but highly oriented,[10] the error in the first

[10] Büssem, Gross and Herrman, *Z. Physik*, **64**, 537 (1930).

interpretation arising as described above. In the present work error from this source was practically eliminated by reflecting the x-ray beam from the surface of a small wire. The degree of curvature is so great that even if the crystals were oriented with respect to the surface of the wire there would be sufficient variation of the orientation to the x-ray beam to insure reflection from many different planes.

Even with these precautions it was often impossible to state definitely whether the deposit was amorphous or crystalline. The presence of at least the two strongest lines of the antimony pattern was taken as evidence that the deposit contained crystalline material. A majority of the specimens examined were evidently mixtures of the two forms, since the complete diffraction pattern of antimony could be brought out by heating above the transition temperature a deposit whose original diffraction pattern showed only two or three of the strongest lines.

The results of this phase of the investigation are shown in Fig. 1. Curves C and A are those of Cohen and Coffin[6] showing the effect of concentration and temperature on the structure of the deposits from aqueous solutions. These curves were determined for current densities of 0.02 and 0.05 ampere per square centimeter, respectively. Since the current density was maintained between these limits during deposition from glacial acetic acid, it is not a significant variable. Curve B indicates the results obtained using glacial acetic acid as the solvent. It appears that for a given concentration amorphous antimony may be deposited from glacial acetic acid at a higher temperature than from aqueous solution, the difference being marked at lower concentrations; while at a given temperature it may be deposited from solutions of lower concentration. The change in solvent apparently has one other effect. Cohen and Coffin imply that the change from amorphous to crystalline antimony is sharp, while in deposits from glacial acetic acid the two forms are mixed over a rather wide range. Only the specimens deposited under conditions furthest from the curve show evidence of being predominantly crystalline; and those indicated in the figure as mixtures contain only a small proportion of the crystalline form.

**Deposition of Arsenic.**—Conditions analogous to those employed in the deposition of antimony were used to effect the deposition of arsenic as a black, lustrous, metallic plate from solutions of the chloride in glacial acetic acid. There appeared to be no tendency toward the formation of "burnt" plates at higher temperatures as noted in the case of antimony. Arsenic trichloride is either very much less ionized, or less solvolyzed in acetic acid than antimony trichloride, since solutions of the former do not conduct as well as those of the latter of the same concentration.

x-Ray diffraction patterns were determined for deposits under extreme conditions of temperature and concentration comparable to those studied in the case of antimony. The method described for antimony was used for

obtaining the patterns and the same precautions were observed to make sure that deposits which gave an apparently amorphous pattern were truly amorphous. There was no question as to the sufficient thickness of these deposits since a film of arsenic could easily be peeled off in many cases, and the plate was often thick enough to prevent diffraction from the base metal. Amorphous diffraction patterns were obtained by transmission of the x-ray beam through a specimen which had been detached from the base metal and more or less broken up, thus definitely eliminating the possibility of an apparently amorphous pattern resulting because of the preferred orientation of the crystals of the deposit. Results of typical runs are given in Table I.

TABLE I

ELECTRODEPOSITION OF ARSENIC FROM GLACIAL ACETIC ACID

| Concentration G. $AsCl_3$ | Concentration G. $HC_2H_3O_2$ | Metal base | Current density amp./sq. cm. | Temp., °C. | Structure |
|---|---|---|---|---|---|
| 12.6 | 87.4 | Cu | 0.0006 | 26 | Amorphous |
| 12.6 | 87.4 | Pt | .006 | 90 | Amorphous |
| 50 | 50 | Cu | .008 | 26 | Amorphous |
| 50 | 50 | Pt | .020 | 90 | Amorphous |

Two crystalline forms of arsenic are known and two amorphous forms have been described.[11] As in the case of antimony the change from amorphous to crystalline arsenic is monotropic and has been reported at about 270° or at 360°. One would expect to be able to control the nature of this deposit near this transition point, as in the case of antimony, by varying the concentration and temperature of the bath. This possibility will be investigated using solvents which will permit the maintenance of the desired temperature range.

**Deposition of Bismuth.**—Bismuth chloride is very much less soluble in glacial acetic acid than are the chlorides of antimony and arsenic. Electrolysis of such solutions results in the cathodic discharge of the metal, but only at low concentrations, low temperatures and low current densities can deposits be obtained which are smooth and adherent. Even under these conditions continued electrolysis results in the formation of a black

TABLE II

ELECTRODEPOSITION OF BISMUTH FROM GLACIAL ACETIC ACID

| Concentration G. $BeCl_3$ | Concentration G. $HC_2H_3O_2$ | Metal base | Current density, amp./sq. cm. | Temp., °C. | Structure |
|---|---|---|---|---|---|
| 6 | 94 | Cu | 0.011 | 28 | Smooth |
| 23 | 77 | Cu | .022 | 29 | Gray, powdery |
| 33 | 67 | Cu | .024 | 29 | Gray, powdery |
| 6 | 94 | Pt | .028 | 95 | Black, powdery |
| 33 | 67 | Pt | .026 | 95 | Black, powdery |

[11] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, Vol. IX, 1929, p. 18.

spongy mass of metal. x-Ray diffraction patterns, obtained in the same manner as described above, indicate that within the limits studied bismuth is deposited as the crystalline metal. Table II gives typical results for bismuth.

Amorphous bismuth has not yet been reported. From analogy one might expect to electrodeposit the non-crystalline form from solvents permitting the maintenance of a much lower temperature.[12]

## Summary

Arsenic, antimony and bismuth may be electrodeposited from solutions of their chlorides in glacial acetic acid.

x-Ray diffraction studies of these deposits indicate that, under the conditions of temperature and concentration studied, arsenic is always obtained in the amorphous form, whereas bismuth is discharged as the crystalline metal.

Antimony may be deposited in either the "explosive" metastable modification or in the crystalline form depending upon conditions of temperature and concentration.

These studies indicate that the solvent must be considered as an additional factor of importance among the conditions which affect the structure of electrodeposited antimony.

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[12] The chlorides of stannic tin, titanium, germanium and phosphorus are quite soluble in glacial acetic acid. Only in the case of tin is the resulting solution appreciably conducting to give a deposit of the metal upon electrolysis. Titanium tetrachloride appears to react with the solvent with formation of a white precipitate. Zinc chloride, though soluble, apparently does not ionize to any large degree in glacial acetic acid. The addition of water, however, increases the conductivity decidedly and leads to the deposition of zinc.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# THE PERSISTENCE AND DEVELOPMENT OF CRYSTAL NUCLEI ABOVE THE MELTING TEMPERATURE

BY WILLIAM T. RICHARDS

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## Introduction

The crystallization of metastable liquids has been the object of considerable study, but has yielded singularly little systematic information. Outstanding in this field are the researches of Tammann[1] and his coworkers which have defined an important relationship between the number of nuclei formed per unit time in a given mass of liquid and the temperature of the liquid. For the purposes of the discussion to follow, the "nuclei number" of Tammann may be expressed in somewhat different terms. If we consider a very large number, $N_0$, of tubes each containing unit weight of metastable liquid at a given temperature, and if after a time $y$ a number $N_t$ of these remain uncrystallized, it is reasonable to suppose these quantities to be related by an expression of the form

$$N_t = N_0 e^{-ft}$$

where $f$, a constant, has the dimensions of a reciprocal time and hence may conveniently be called the crystallization frequency of the substance at the temperature of observation. The investigations of Tammann have established that $f$ passes through a maximum with decreasing temperature, and that this maximum does not necessarily coincide with that of the linear crystal growth velocity.

It will be profitable to examine more closely the conditions under which $f$ may be expected to be independent of time. If we consider a large volume of homogeneous metastable liquid at uniform temperature, and divide the volume into imaginary elements of unit weight, the constancy of $f$ among these elements follows from the kinetic theory of heat, since it implies only that the probability of formation of a crystal center is the same in each element. If the imaginary boundaries are replaced by glass walls no change can occur provided that the walls are indifferent to the crystallization process, and provided that the condition of the liquid in each tube remains identical. If, however, the tubes are subjected to different conditions, as, for example, a considerable alteration of temperature, there is no reason to suppose, *a priori*, that the crystallization frequency will be unaffected when the initial temperature is reëstablished. This is at once apparent when it is remembered that the metastable liquid is not in equilibrium. The constancy of $f$ will be destroyed if the liquid, in passing from one temperature to another, must undergo a molecular adjustment which is not more rapid than that necessary to form a crystal center.

[1] G. Tammann, "Aggregatzustande," Leipzig, 1922, summarized in Chapter IX.

Experimental evidence is at hand which indicates that one of the factors influencing the crystallization frequency is the treatment of the liquid previous to undercooling. Othmer[2] observed that the number of crystal centers in piperonal and several other substances diminished as the liquids were raised increasingly above their crystallization temperatures. He further reports that, with fatty acids and their esters, the nuclei number increases rapidly with time. Hinshelwood and Hartley[3] have noted, in apparent contradiction to Othmer's second result, that a far greater number of tubes containing salol and *p*-toluidine crystallized immediately on undercooling than was consistent with a simple explanation based on probability; they have found, in other words, that $f$ is a function of time. Like Othmer they also observe a diminution in tendency to crystallize with increased preheating of the liquid. In support of these systematic investigations there is a quantity of vague laboratory experience. The increased supercooling of non-metals and metalloids if their melts are strongly heated seems, for example, to be generally recognized. The control of grain number and size by heat treatment of the fused metal is becoming an important factor in the manufacture of steel and alloys. Again, it is habitually found with glycerin and many of the sugars that, whereas the initial crystallization is a matter of considerable difficulty, subsequent recrystallizations occur readily enough even when the substance has been raised many degrees above its melting temperature.

A number of explanations are available for this behavior, but none to date is wholly free from objection. The hypothesis of Othmer, which is supported by Tammann,[1] postulates the existence above the melting point of what may be called a "memory" of the crystalline condition. Loose aggregates, the nature of which is not clearly defined, but which possess at least some of the anisotropic characteristics of crystals, are supposed to exist in the melt, and to be destroyed increasingly with increasing temperature. This explanation assumes that the velocity of transition between the liquid and pseudo-crystalline states is slow compared to that between the pseudo-crystalline and the crystalline, a condition which it is not impossible to imagine. Apparent partial support to such a view is given by recent evidence concerning x-ray diffraction in liquids.[4] This hypothesis cannot, however, be accepted without reserve. If aggregates of this kind exist in a liquid raised only a few degrees above its melting point, its thermodynamic properties must differ from those of a more strongly preheated liquid at the same temperature and experimental evidence for this difference is entirely lacking. Furthermore, if this hypothesis is accepted it is necessary, on the basis of experimental evidence, to suppose

[2] P. Othmer, *Z. anorg. Chem.*, **91**, 209 (1915).

[3] C. N. Hinshelwood and H. Hartley, *Phil. Mag.*, [6] **43**, 78 (1922).

[4] G. W. Stewart, *Phys. Rev.*, **32**, 558 (1928).

that the crystal state itself may be dual, one modification being metastable to another, for it will be demonstrated below that several liquids which are deactivated by preheating may be crystallized without regaining their activity, for this reason the explanation of Tammann and Othmer will be supposed, in this communication, to be of limited applicability and reserved for cases inexplicable by other hypotheses.

A second hypothesis, advanced by Herzfeld[5] to explain Othmer's results and consequently applicable also to those of Hinshelwood and Hartley, is based on adsorption. Herzfeld supposes that the primary liquid may contain impurities which are adsorbed on small crystals to such an extent that their free surface energy becomes actually negative. Since this means that less work is necessary for the crystals to maintain their lattice than to become liquid, they do not melt until their temperature has been raised considerably above the true melting point. Such an explanation seems in high degree improbable, since under these conditions solid solution could scarcely fail to take place. Again, the interfacial tensions of the substances investigated by Othmer are low, and they cannot, therefore, adsorb strongly. Furthermore, such a system should, on crystallization and remelting, undergo an identical cycle, which is not substantiated by experiment. Finally, the experiments of Tammann[6] and others[7] show that the presence of strongly adsorbed foreign materials tends to inhibit the growth of crystals. This hypothesis will receive further consideration in the experimental section.

A third explanation, of an obvious character, which does not appear to have been previously suggested, is that crystals of isomorphous impurities of melting point higher than that of the substance under observation are contained in the liquid. At a sufficiently high temperature these melt and undercool in turn. If the liquid is subsequently crystallized mixed crystals are formed which are destroyed by melting the primary substance, and the impurities are then evaporated from the crystal form in the state of an undercooled solute. This explanation appears improbable for the type of phenomenon observed by Othmer, since he found that the number of nuclei progressively diminished with increasing temperature, and not that the crystallization of the liquid abruptly ceased at a critical point. It will further be shown experimentally that the activity of the agent producing crystallization may be increased by suitable treatment above the melting point of the primary substance, a fact which it is difficult to explain by this hypothesis. The presence of isomorphous impurities will not, therefore, be advanced as a general explanation.

[5] K. F. Herzfeld, "Colloid Symposium Monograph," Vol. VII, 1930, p. 51.

[6] G. Tammann, "Kristallisieren und Schmelzen," Leipzig, 1903.

[7] A comprehensive bibliography is given in H. Freundlich "Kapillarchemie," Leipzig, 1923, p. 448.

A fourth explanation for the influence of preheating on the melt is due to Hinshelwood and Hartley, who ascribe it to decrease in the catalytic activity of colloidal dust particles derived from the air. These are considered to be surrounded by an oriented adsorbed layer, the system thus formed taking the place of a fragment of pure crystal in discharging the undercooled liquid. If large enough the system is effective immediately; if not, a series of fortunate chances is necessary to build it to the necessary size. The degree of dispersion of the active colloidal particles is supposed to change irreversibly with preheating, time, and other experimental conditions, thus accounting, *ad hoc*, for any observed behavior. In general, this explanation appears the most satisfactory of the four. Indeed, it may be considered that the explanation supported below is a revision of that of Hinshelwood and Hartley, although it retains few points of similarity. Much unsatisfactory vagueness concerning catalysis and adsorption has been removed by the accumulated knowledge of nine intervening years. For this reason a further discussion of the viewpoint of Hinshelwood and Hartley, which would add inordinately to the bulk of this communication without materially increasing its value, will not be attempted.

An hypothesis of a more specific character appears to be at present possible. The liquid may be supposed to contain minute particles of an active adsorbent, the adsorption space of which may be filled with liquid or crystalline adsorbate depending on its previous treatment. If, now, the reasonable assumption is made that the entropy change of the transition from free liquid to free crystal is not greatly different from that of adsorbed liquid to adsorbed crystal, and it is further postulated that in certain cases the heat of adsorption of the crystalline adsorbate is greater than that of the liquid, a plausible explanation for the results obtained by Othmer and by Hinshelwood and Hartley at once emerges. If the adsorption space contains the crystalline modification its heat of adsorption will, in effect, be added to the melting heat of the free crystal in opposing the destruction of the lattice by thermal agitation, and the melting temperature of the crystalline adsorbate will be above that of the pure crystal. The crystalline arrangement may, therefore, persist above the ordinary melting temperature of the solid, and grow into the liquid if the temperature is subsequently lowered. There is no reason to suppose, however, that the rate of crystal growth in the liquid adsorbate will be identical with that in the free liquid at a given temperature. It is only necessary for it to produce normal crystals more rapidly than they are produced by the spontaneous crystallization of the free undercooled liquid for the presence and growth of the crystalline adsorbate to be the decisive factor in crystallization. In cases cited below the apparent crystallization frequency is increased over a million-fold owing to this process. At a temperature somewhat above the true melting point the crystal form of the adsorbate will be destroyed, and

the germ, therefore, deactivated. After this the apparent crystallization frequency of the liquid may diminish very greatly. While no statement can be made concerning the spontaneous tendency to crystallize in the adsorption space, it is easy to imagine cases where this will not be very different from that of the pure liquid.

It is apparent that the heat of adsorption referred to above is not easily accessible to experiment, for adsorption isobars cannot be obtained. If the vapor pressure against temperature lines for liquid and crystal are drawn as in Fig. 1 only one point, D, on the liquid line AB, that representing the temperature above which the germ loses its activity, may be observed. The slope of the line, DE, which represents the vapor pressure of the most strongly held crystalline adsorbate as a function of temperature, cannot be directly obtained. There appears, instead, the apparent paradox that from D to the true melting point B the crystalline adsorbate is identical in activity with the liquid. That this situation presents, in fact, no serious difficulties in interpretation is due to the researches of Taylor[8] on the complexity of adsorbing surfaces, and the theoretical treatment of adsorption given by Polanyi.[9] As a result of these it is now generally agreed that the adsorption volume is filled with material bound by widely different adsorption heats. It is quite reasonable to suppose, therefore, that, as the temperature is progressively raised above the melting point, crystalline material evaporates from the adsorption space progressively from lower to higher heats of binding, the crystalline adsorbate being replaced by liquid. When, at a sufficiently high temperature, crystal form is finally obliterated in the adsorption space, the liquid adsorbate may be supposed to differ importantly from the free liquid in crystallization frequency only because the former becomes metastable below the deactivation temperature, whereas the latter becomes metastable below the true crystallization temperature. At any point below the deactivation temperature any crystalline adsorbate present may develop, with a velocity which cannot be predicted, until it attains a vapor pressure identical with that of the free

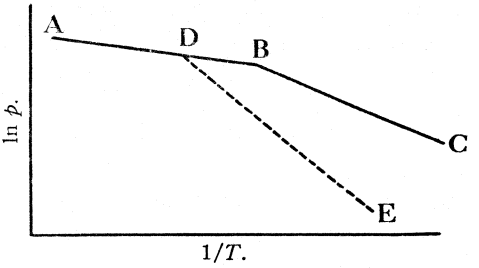


Fig. 1.—Vapor pressure–temperature diagram for liquid, crystal, and crystalline adsorbate. AB represents the vapor pressure–temperature function of the liquid, BC that of the crystalline solid, and DE that of the most strongly bound portion of crystalline adsorbate. B and D give the melting and deactivation temperatures, respectively.

[8] H. S. Taylor, *Proc. Roy. Soc.* (*London*), **A108,** 105 (1925).

[9] M. Polanyi and co-workers, *Z. physik. Chem.*, **132,** 321 (1928), and subsequent papers.

liquid. If the free liquid happens to be below its crystallization temperature, crystallization of the entire system, of course, results.

This point of view, if it can be experimentally substantiated, is capable of explaining in some detail the observations of Othmer and of Hinshelwood and Hartley. In both these cases the active adsorbents were introduced by accident, and were, therefore, presumably of diverse character. It is not to be expected, in view of this, that they should all be cleared of crystalline adsorbate at the same temperature. The destruction of the activity of the adsorbent by aging which is noted by Hinshelwood and Hartley indicates, perhaps, that relatively few active spots were present in each portion of liquid, and that in time these became overlaid with traces of dissolved impurities more strongly adsorbed than the crystalline adsorbate. Even the apparent contradiction, that Othmer notes increase in nuclei numbers with time, whereas Hinshelwood and Hartley report that fewer portions of undercooled liquid crystallize after a few hours than at first, is easily resolved. For Othmer's observation times were only a few minutes whereas Hinshelwood and Hartley carried on their experiments for several days. Both were observing the effect of the development of the crystalline adsorbate below its melting temperature, a process which may take several minutes to become manifest under a microscope at temperatures not far from the melting point, but which, in most cases, would be essentially complete after a few hours.

## Experiments with Salol and Benzophenone

**Methods and Choice of Substances.**—The method of Hinshelwood and Hartley is preferred to that of Othmer because it permits sealing the material under observation in glass tubes, and, therefore, removes all possibility of subsequent contamination. It imposes, however, severe restrictions. The substances studied must, first of all, be capable of prolonged undercooling in order that the effect of adsorbents may be distinguished from the spontaneous crystallization of the liquid. Secondly, they must be stable at temperatures far above their melting points, because strong preheating is necessary to deactivate the adsorbents, and if important decomposition takes place during this process, the conditions on recooling will not be reproducible. Again, convenience dictates that the melting temperature should be higher than 23° because many degrees of supercooling are necessary to make the phenomenon clearly manifest, and prolonged maintenance of constant temperature baths below 0° is a laborious and expensive undertaking. Finally, the substances must be obtainable in large quantity and in a reasonably pure state.

Of some twenty compounds examined only two were found suitable. Most others decomposed before the adsorbent could be deactivated, or showed too high an apparent spontaneous crystallization frequency.

Salol (phenyl salicylate, melting point 42°) and benzophenone (diphenyl ketone, melting point 48°) were found satisfactory on all the counts given above, and had several additional advantages. Each of them is known to exist in several crystalline modifications, but these were readily recognizable by eye. The monoclinic modification of benzophenone, which melts at 27°, has a growth velocity[10] far less than that of the stable,[11] whereas the unstable modification of salol, which melts at 39°, has been found to grow with only one-fourth the rapidity of the stable.[10] Other modifications of benzophenone were not observed. A third modification of salol not previously known, which melts at 31°, was found to grow even less rapidly than the two others at 25°. Where doubt existed a rough measurement of the melting point at once decided which modification was present.

Since the argument under consideration may be tested by a series of critical experiments, these will be reported separately, and numbered for the sake of convenience.

**Experiment 1. Spontaneous Crystallization Frequency.**—Twenty sealed tubes, each containing 3 g. of U. S. P. salol, were subjected to a temperature of 130° for one hour. They were then kept for a month at 25°, in which time none had crystallized. An exactly similar experiment with benzophenone yielded an identical result.

One hundred fifty grams of salol, and a similar quantity of benzophenone were separately distilled into large tubes which had been carefully freed from dust by repeated distillations of water *in vacuo*. Both substances were distilled *in vacuo*, and as nearly as possible without ebullition. The salol distillation was accompanied by decomposition, but not in important amount. Both the tubes so prepared remained for six months at 25° without crystallization.

From this experiment it is concluded that the spontaneous crystallization frequencies of salol and of benzophenone are small.

**Experiment 2. Accidental Inclusion of Adsorbents.**—Twenty sealed tubes containing 3 g. each of U. S. P. salol were raised above the melting point to a determined temperature, kept there one hour, and then returned to 25° for two hours. This process was repeated, raising the preheating temperature progressively. At each temperature the contents of one or more of the tubes failed to crystallize in the allotted time. Such a tube was considered partially deactivated, but not removed from the experiment. The percentage of tubes partially deactivated plotted against the number of degrees by which the preheating temperature exceeded the melting point is given in Curve A, Fig. 2. A different sample of U. S. P. salol, which was considered to have somewhat higher purity than the first because more nearly colorless when fused, gave the result represented by Curve B, Fig. 2.

An exactly similar experiment with C. P. benzophenone yielded the result indicated by Curve A, Fig. 3. With both salol and benzophenone the contents of a tube, once partially deactivated, remained so throughout with few exceptions. These are accounted for under Experiments 5 and 7.

Experiment 2 is believed to indicate that commercially obtainable salol and benzophenone contain active adsorbents. The fact that different samples of salol showed

[10] Tammann, Ref. 6, p. 146 ff.

[11] Von Pickardt, *Z. physik. Chem.*, **42**, 17 (1902).

different deactivation temperatures is somewhat against the explanation of his experiments accepted by Othmer, and may be interpreted in favor of that of Herzfeld. Against

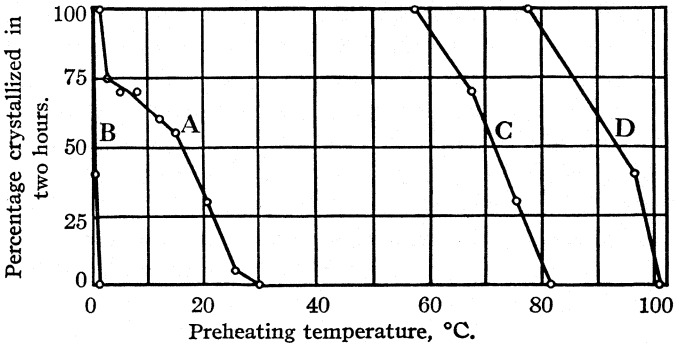


Fig. 2.—The influence of preheating on the crystallization of tubes containing undercooled salol. Curves A and B were obtained with different samples of U. S. P. salol, Curve C with salol containing powdered crystalline quartz, and Curve D with salol containing active charcoal. The "preheating temperatures" represent the number of °C. above the melting temperature to which the various samples were subjected before being supercooled. In this figure, as in Fig. 3, the lines connecting experimental points have little significance, and are included merely to clarify the diagram.

both it must be noted, however, that relatively large volumes of substance from the same sample behaved quite differently, which points toward minute heterogeneous impurities.

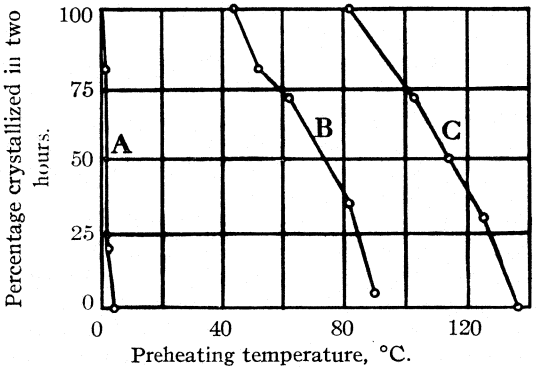


Fig. 3.—The influence of preheating on the crystallization of tubes containing undercooled benzophenone. Curve A was obtained with C. P. benzophenone, Curve B with benzophenone containing active charcoal, and Curve C with benzophenone containing powdered crystalline quartz.

**Experiment 3. Rate of Crystal Growth in the Adsorption Space.**—The twenty partially deactivated tubes containing salol which were obtained in Experiment 2 were kept at 25° for one month, being observed every twelve hours during this time. They crystallized at the rate, which was maintained with surprising constancy throughout, of 8% of the tubes present in ten hours. A similar set of observations with the benzophenone from Experiment 2 yielded somewhat similar results, but the percentage crystallizing in ten hours was considerably greater in the early stages of the experiment.

It may be concluded from this that a reasonably constant value for $f$ in the equation given above may be obtained by a mechanism quite other than fluctuation phenomena in the liquid. For Experiment 1, which is in every way identical except for the extent of preheating, yielded no crystallization in a time sufficient for the

tubes wholly to crystallize in Experiment 2. Important decomposition at 130° could not have taken place for the salol crystallized with a normal velocity, and had changed less than 0.1° in melting point. Othmer's explanation cannot be accepted in view of the behavior of benzophenone, which confirms the results obtained by Hinshelwood and Hartley. It is convenient, therefore, to suppose that the crystal form had never entirely disappeared from the system, and that its gradual growth ultimately inoculated the undercooled liquids. At the normal growth velocity of crystalline salol any tube would have been filled under the conditions of the experiment in five minutes. The growth velocity is therefore, greatly retarded. We may suppose, with Herzfeld, that this is due to adsorbed impurities, or, alternatively, that the growth velocity in the adsorption space is far less than in the free liquid. The enormous time intervals involved and the differences in behavior of different samples of the same substance seem to favor the latter hypothesis. The regularity in the rate of crystallization of the tubes merely indicates that the impurities are included at random.

**Experiment 4. The Effect of Various Adsorbents.**—The results of Experiment 2 indicate that different substances have different powers of maintaining the crystal form of the adsorbate above the melting temperature. Three classes of these may be predicted: those for which the difference between the crystalline and liquid adsorption heats is positive, when preheating will be necessary to greatly supercool the liquid; those where this difference is negligible, which will be indifferent to the crystallization process; and those where it is negative, when the transition from crystal to liquid adsorbate will occur below the true melting temperature. The last class has no practical importance, since a crystal may be superheated only under very unusual conditions. Only the first class will be considered here.

In order to test the effectiveness of various substances in this respect, salol and benzophenone were separately ground with various possible adsorbents. Sets of three sealed tubes were prepared for each adsorbent with both salol and benzophenone, roughly 0.5 cc. of adsorbent and 3 cc. of primary substance being included in each tube. They were then raised above the melting points in progressive steps, the temperature above the melting point at which partial deactivation was first observed in a single one of the set of three containing a given adsorbent being noted in Table I as the partial deactivation temperature. Since these temperatures are neither exactly defined nor clearly reproducible they have been quoted to the nearest 10° only.

TABLE I

PARTIAL DEACTIVATION TEMPERATURES FOR VARIOUS ADSORBENTS WITH SALOL AND BENZOPHENONE

| Adsorbent | Mercury | Ignited ferric oxide | Brass filings | Pulverized mica | Ground Pyrex | Roll sulfur | Silica gel | Powdered quartz | Active charcoal |
|---|---|---|---|---|---|---|---|---|---|
| Salol | 10 | 10 | 10 | 80 | 80 | 60 | 80 | 110 | 150 |
| Benzophenone | 10 | 10 | 10 | 50 | 70 | 50 | 70 | 140 | 110 |

Deactivation temperatures of 10° or less may mean complete inactivity since the primary materials may contain active adsorbents as impurities. The experiments with sulfur are not satisfactory, since it causes both salol and benzophenone to undergo chemical change.

Since it was evident that active charcoal was extremely effective in preserving the crystalline modification, several brands, which were obtained through the courtesy of Professor Edward Mack of The Ohio State University, were tested for their relative activities. The least active, a Holland norit was partially deactivated with salol 40°, and with benzophenone 70°, above the melting temperature. The most active of

eighteen varieties tested bears the trade name of Nuchar, and its partial deactivation temperatures are given in Table I.

This experiment is taken to indicate that different adsorbents have different powers of retaining the adsorbate in crystalline form, and the difference is interpreted as due to differences in the adsorption heats of crystal and liquid. In the light of the extraordinary divergence of their behavior, it seems that the interpretations of Herzfeld and Othmer should be further considered only when the absence of such adsorbents is definitely proved.

It may not be at once apparent why it is possible to supercool a liquid in a glass tube after a preheating of only 10° or less when powdered glass is not deactivated without preheating some 70°. The reasonable explanation is two-fold: firstly, the active spots in the complex surface of the glass tubing have been obscured by the aging of the tube by adsorption, evaporation, slow surface reactions and the like, and secondly, when the adsorption space of the glass is filled with gas, intimate contact between crystals and the adsorbent is prevented. If the liquid is carefully deactivated by gentle preheating and adsorbent added without contact with crystalline material no activation of the adsorbent is observed until the metastable liquid is crystallized at low temperature, after which the normal course of events is established. Grinding crystals with adsorbent is, of course, the most effective means for securing activation.

**A Detailed Study of Quartz and Carbon.**—Since active charcoal appears the most effective of the adsorbents, and since crystal quartz is that least likely to cause chemical action or introduce impurities, a somewhat closer scrutiny of their behavior was undertaken. Using the method of sealed tubes, and supercooling at 15° for two hours or more after each preheating, Curves C and D, Fig. 2, and Curves B and C, Fig. 3, were obtained. After the deactivation process was complete, melting point determinations on representative samples of the various mixtures were made. The benzophenone–quartz system showed no change, and the benzophenone–carbon mixture had dropped only 0.3° as a result of its preheating. This change may be attributed to impurities introduced by the active charcoal. The salol–quartz system showed no decomposition by the melting point method, but the salol–carbon system, which had been subjected to 150° for fifteen minutes, showed a drop of 1.0°, too much to be due to impurities from the charcoal. Several independent experiments demonstrated that this decomposition was not due to the presence of the charcoal, but that at the temperature necessary for deactivation enough decomposition of salol always occurred to lower its melting point at least 1°.

A word should be said concerning the time of heating necessary to produce deactivation. At temperatures above 130° partial deactivation usually occurs in the time necessary to bring the melt of salol or benzophenone to the bath temperature. For example, a set of ten tubes containing charcoal and benzophenone were immersed for fifteen minutes in a bath at 110°. On cooling to 15° one of these resisted all attempts to produce crystallization at this temperature. The tubes were then kept at 110° for three days. On recooling to 15° exactly the same result was obtained. Similar persistence of the tendency to crystallize with benzophenone–quartz was observed, but the decomposition of salol at high temperatures made a repetition of this experiment with that substance futile.

It should also briefly be noted that 0.5 g. of carbon required a definitely higher temperature for deactivation than did 0.01 g. This indicates either that very active spots are rare with this adsorbent or that adsorption equilibrium has not been established over a greater part of the surface. The rather indefinite character of the deactivation temperature must be due to the same cause.

**Experiment 5. Development of Crystal Form Above the Melting Temperature.**—

Since crystal growth in the adsorption space is greatly retarded it is possible, as has been demonstrated by Experiment 2, for a volume of liquid to remain undercooled for many days and yet finally to crystallize owing to the presence of active adsorbents. If the velocity of the liquid-crystal transformation in the adsorption space increases with temperature and the adsorption space contains undercooled liquid adsorbate above the melting point, it should be possible to develop the crystalline adsorbate above this temperature more rapidly than at a temperature at which the free liquid is undercooled.

Experiments of this type have been carried out with salol and benzophenone, using both charcoal and quartz as adsorbents, although they are somewhat more striking with the former. In a representative experiment twenty tubes containing salol–charcoal in an activated condition were heated at 135° for thirty minutes, and undercooled to 15° for two hours. During this time eight crystallized, the others being partially deactivated. All the tubes were then kept at 100° for one hour and returned to 15°, upon which twelve tubes crystallized immediately. The eight tubes here remaining uncrystallized may be considered deactivated. The distinction between partial deactivation and deactivations thus acquires a clear-cut meaning: partial deactivation indicates that crystalline adsorbate cannot develop into the undercooled liquid within two hours at 15° and deactivation implies that the adsorption space has been cleared of crystalline adsorbate. The distinction between the two is conveniently established by development of the crystalline adsorbate some 50° above the melting temperature, and this method was consistently used to ascertain whether or not crystal form had disappeared from the system.

This experiment is a powerful support to the conception of complexity of the adsorbing surface which was found necessary in the introduction. Furthermore, by demonstrating the partial reversibility of the adsorption process, the experiment makes reasonable the assumption that, in some cases, adsorption equilibrium is attained between crystalline adsorbate and liquid above the melting temperature. Finally, the points of view of Othmer and Herzfeld cannot account for these results in a straightforward manner.

**Experiment 6. The Activation Energy of Adsorption.**—It has been demonstrated in Experiment 5 that the crystalline adsorbate develops more rapidly at high temperatures than at low. It is customary to interpret behavior of this kind in terms of an activation energy. In view of the success of recent work of Taylor[12] on diatomic gases, where the theory of activated adsorption was developed for the first time, it becomes of interest to inquire whether other means of demonstrating that an activation energy is required for adsorption of the crystalline modification may be devised. One has met with partial success, although it leaves much to be desired in elegance.

Ten tubes containing salol and carbon, which had been prepared by mixing the two after the salol had been deactivated in order to avoid decomposition attendant on strong preheating, were crystallized by eight hours' immersion in a solid carbon dioxide–acetone mixture. Of these, five were removed and held at the crystal–liquid transition temperature of salol for eight hours, the others being kept at low temperature during this time. All ten tubes were then plunged into a bath at 60° and melted as rapidly as possible. After an hour's immersion at 60° all of the five developed at the melting point, and only one of the five kept at low temperatures crystallized at 15°. This experiment was frequently repeated with variations, and, although sufficient activity could always be restored by treatment at the melting point, a small percentage of the tubes kept at low temperatures always showed activity. With benzophenone no conclusive results were obtained, probably because of its higher crystal growth velocity. The weakness of the method lies, of course, in the necessity for carrying the salol through its melting

[12] H. S. Taylor, THIS JOURNAL, **53**, 578 (1931).

temperature, at which the crystalline growth velocity into the adsorption space is presumably considerable, before it can be preheated.

Experiments 5 and 6 together are considered as a strong indication that the adsorption of the crystalline modification is a process requiring an activation energy. Experiment 6 alone is the final piece of evidence to be advanced in this communication against Othmer's and Herzfeld's viewpoints since, after crystallization, the germ-forming ability of a substance is not immediately regained.

**Experiment 7. The Effect of Shaking and of Supersonic Waves.**—When a system is deactivated shaking has no effect whatever, but when partially deactivated shaking may strikingly accelerate crystallization. For example, ten sealed tubes containing benzophenone and activated quartz powder were kept for one hour at 100° and allowed to cool slowly to room temperature. After eight hours at 25° they showed no signs of crystallization and might be examined, and even mildly agitated without crystallization. Violent shaking sufficed, however, instantly to crystallize the liquid. With other systems the effect of shaking was often similarly manifest; in some cases it could cut days from the duration of the undercooled condition.

An explanation for this behavior at once suggests itself in terms of the adsorption layer. If this consists of crystal obscured by liquid adsorbate the momentary removal of the latter would permit access of the free liquid to the inner adsorption space, and hence greatly accelerate crystal growth. If the onset of turbulence in the undercooled liquid is accompanied by violent shearing forces at the surface of the adsorbent, it is reasonable to suppose that crystalline adsorbate might thus be made momentarily accessible to the free liquid. This explanation, while in high degree tentative, is partially confirmed by the effect of high intensity sound waves where turbulence may be secured with very little mechanical displacement. Supersonic waves have an effect exactly parallel to that of shaking, being somewhat more effective when the adsorbent is present in traces and somewhat less when it is present in bulk, as is to be expected, but being totally without effect on deactivated systems.

**Miscellaneous Experiments.**—Several points which have no bearing on the main argument must be briefly mentioned to give completeness to the work. Benzophenone–charcoal systems showed an enormously enhanced tendency to crystallize from a state of partial deactivation if rapidly cooled. A complete picture of the effect of a sharp temperature gradient between adsorbent and free liquid on the material in the adsorption space will doubtless emerge only after more intimate knowledge of the latter becomes available.

Crystallizations at low temperature deserve a word of mention. It is believed that this occurs wholly owing to the so-called Helmholtz process which consists of the formation by fluctuations of a crystal nucleus of sufficiently small vapor pressure for continued growth. If the conclusion of Experiments 5 and 6, that the development of the crystalline adsorbate requires a considerable activation energy, is correct, no other cause for the crystallization of undercooled liquids at low temperatures is apparent. Benzophenone crystallized readily when just above its glassy state, giving generally the stable rhombic modification. Salol, when undecomposed, gave the stable modification at about −90° in about 95% of the cases observed. When its melting point has been lowered as little as 1°, however, by ten minutes' heating at 160° in the presence of carbon, an unstable modification with a melting point of about 31° and an extremely low growth velocity at 15° was almost invariably obtained at −90°. The transition of this modification to the stable form after inoculation was an extremely slow process, and mechanical disturbance without inoculation appeared to cause a transition to the 38.8° modification noted by Tammann, although this was not definitely established.

Occasional cases were noted in which a drop of 10° produced immediate crystalliza-

tion in one or two of a large number of tubes which had remained strongly undercooled for a long period. Thus of twenty sealed tubes containing U. S. P. salol, which had stood at 25° for three weeks after apparent deactivation at 100° for one hour, one crystallized at once when the temperature was lowered to 10° and no more crystallized after twelve hours at this temperature. If it is true that the development of the crystalline adsorbate proceeds less rapidly at low temperatures than at high, another cause must be assigned to this phenomenon. This appears from the Helmholtz expression which indicates that the radius of the smallest particle which may act as a crystallization center diminishes with diminishing temperature. If the undercooled liquid contains an active adsorbent on which a crystalline area of less than the critical radius at one temperature has developed, this area may exceed the critical radius at a somewhat lower temperature and produce immediate crystallization. The crystalline adsorbate is wholly prevented from evaporation by the adsorption heat and remains, so to speak, in a stationary state in the undercooled liquid without the ability to develop into the latter. This situation, although theoretically straightforward, occurs relatively seldom in practice, and, as might be expected, only under special conditions of pretreatment like those described above.

## Experiments with Other Substances

**Slowly Crystallizing Liquids.**—Although the microscopic technique originating with Tammann is not capable of as rigorous interpretation as the sealed tube method, it is more economical of both time and material, and may be applied to any substance of small crystal growth velocity. The reëxamination of all the substances thus studied by Tammann and his school is indicated, but was not undertaken because it was felt that the generality of the thesis here supported would be little advanced by knowledge of a class of substances with properties so highly specialized. An investigation of substances of low molecular weight, whose heats of adsorption are far inferior to those here considered, is essential. It should be possible to develop a method more rigorous and general for this purpose than any at present at hand, and a further test of the reasoning will hence be postponed. The microscopic technique, suitably modified, was therefore applied only to three substances, two of which are important because of the work of previous investigators, and the third because its properties are quite different from any other included in this survey. Piperonal and *p*-toluidine, both of which gave promising indications by the sealed tube method, but neither of which could support without decomposition the preheating necessary to secure deactivation, gave satisfactory results. In the former charcoal produced about twenty more germs per unit weight than the untreated substance, and silica gel about five. In the latter the ratios charcoal, silica gel, and untreated substances were approximately 20:3:1. These quantities varied, of course, within wide limits depending on the quantity of adsorbent and the nature of pretreatment. Acetamide, because of its high crystallization velocity, did not permit counting the nuclei formed, but undercooled consistently to far lower temperatures if charcoal were not present. Silica gel and the pure substance showed

little difference in behavior. In no case was a birefringent adsorption layer observed with low magnification.

**Supersaturating Solutions.**—It appeared of interest to inquire whether similar persistence of crystal form above the transition temperature occurred with crystalline hydrates. To determine this a brief study of sodium acetate was undertaken, which answered this question in the affirmative. Similar indications were obtained with sodium thiosulfate, although these will be omitted to conserve space. A slight alteration in technique was found necessary, the sealed tubes being slowly rotated in a revolving rack in the constant temperature bath in order to accelerate solution.

The solutions of sodium acetate were prepared in lots of twenty sealed tubes as before with salol and benzophenone. After the first attempt the concentration was made consistently 12 *M* in order to prevent the separation of the unstable anhydrous modification. Experiment 2 of the previous section was paralleled with two lots of material obtained from different sources. Using the first lot 100% of the solutions crystallized when preheated 2° above the transition temperature of the trihydrate, only 35% with 3.5° above this, and only 5% with 7.0° preheating. The solutions were kept at room temperature in the intervals between preheating, and slowness of development in the adsorption space was observed as in Experiment 3, the maximum time noted for the development of a crystallization center being nine days. With this sample of sodium acetate it was found possible to parallel Experiment 5 by reactivating a partially deactivated adsorbent at a lower preheating temperature than that which had produced partial deactivation. The second lot of sodium acetate was 100% partially deactivated by 1° of preheating, and, although two of the twenty solutions crystallized after sixteen hours, no further experiments were attempted. Both samples were cleared of the trihydrate by one hour's preheating at 100°, and none of sixty tubes so treated crystallized in eighteen months at room temperature, showing that the spontaneous crystallization frequency of the trihydrate is low.[13] On recrystallization at low temperature only one of the adsorbents was reactivated by three hours' immersion in a bath at 45°. An attempt to find an active apolar adsorbent met, however, with virtual failure. Active charcoal appeared capable of sustaining preheating up to 1°, and sulfur

[13] The recent letter of W. W. Conner in THIS JOURNAL, **53**, 2806 (1931), is confirmed by the observation that, in a few of the solutions made more than 12 *M*, the crystalline anhydrous modification remained eighteen months in contact with supersaturated solution without producing the trihydrate. Similar observations, over far shorter periods, are recorded above for salol and benzophenone, and have been made with sodium thiosulfate. It is quite in accord with the point of view expressed above that the presence of crystals not isomorphous with the stable modification should be as inactive as the glass walls. It should further be noted that growing crystals, which are known to possess great adsorptive powers, are thus proved also indifferent.

had a definitely positive effect but underwent chemical change with the acetate solution. Polar adsorbents were avoided in order to prevent phenomena akin to isomorphism.[14]

## Possible Applications

An attempt has been made in the preceding sections to demonstrate the persistence and development of crystal form above the melting temperature as clearly as possible with the limited means available. It cannot be claimed that the phenomenon has more than academic interest at present except for the explanation of the behavior of metastable liquids. It seems possible, however, that a number of other phenomena may profitably be examined from this viewpoint. Some of these will be discussed briefly below, it being understood that the suggestions which follow are based on little or no experimental evidence, and are merely intended to indicate directions in which further research may be desirable.

Perhaps the most obvious application of this viewpoint is to the purification of materials. It will be seen at once that beyond a certain point recrystallization is merely the most effective method of concentrating foreign material in the substances undergoing purification. Thus, Tammann reports a four-fold increase in the number of nuclei formed per gram of betol after three recrystallizations.[1] This he attributes to greater purity of material, but it seems equally likely that it is due to concentration of active nuclei. This is especially probable since those products which tend to inhibit crystal growth are adsorbed on growing crystal faces, and are, therefore, unlikely to be removed by crystallization. In view of this the most satisfactory procedure for purification by recrystallization is seen to be the discarding of all crystal centers which form immediately. This has the added advantage of removing impurities readily adsorbed by the growing crystals. It is also seen to be advisable to digest the material for some time just below its melting or transition point.

The application of this viewpoint to devitrification is also at once apparent. Evidently a substance which it is desirable to maintain for long periods of time in a vitreous state should be heated far above its softening point. Conversely it should easily be possible to devitrify difficultly crystallizable glasses by the introduction of active germs which have been obtained from the crystalline condition but maintained thereafter above its melting point. The case of glycerin at once suggests itself: the melting point of this substance is too low to permit its maintenance in the solid condition at room temperature. If, however, a suitable activated adsorbent is sealed with liquid glycerin in a glass tube it should crystallize immediately upon cooling even although the temperature of the preparation has greatly exceeded the melting point.

[14] C. A. Sloat and A. W. C. Menzies, *J. Phys. Chem.*, **35**, 2005 (1931).

Again, it seems probable, as previously suggested, that the supercooling of non-metallic and metalloidal melts may be profoundly influenced by similar phenomena. The reasoning given during the discussion of devitrification might in some cases profitably be applied even to the development of grains in metals and alloys.

The experiments outlined above throw grave doubt on the observations of Tammann concerning the quantitative relation between the velocity of formation of crystal nuclei and temperature and appear to disqualify many of his "nuclei number" measurements, since the preheating conditions which he describes are inadequate to deactivate any adsorbing germs which might have been present. Othmer and Tammann both report influence of metals and solid powders on the "nuclei number" without, apparently, at all appreciating the significance of their results. A systematic reëxamination of the question of crystallization frequency in the absence of active adsorbents should clearly be undertaken.

Some manifestations of the so-called Law of Stages may be supposed to be due to a similar mechanism. If we suppose activated adsorbing germs in a system capable of two crystalline modifications, it seems entirely reasonable to suppose that the stable modification of the germ will undergo a transition to the unstable at a temperature somewhat above the true transition temperature. Thus, it may be demonstrated with sodium acetate and sodium thiosulfate of suitable concentration in sealed tubes that, when these are heated ten degrees above the transition point, an unstable modification soon makes its appearance, whereas, heated fifty degrees above the transition point, they remain without crystallization for long periods. Of course, this cannot be the sole important factor, for the spontaneous crystallization frequencies of the stable and unstable modifications are in many cases wholly different, as it is easy to demonstrate with sodium acetate. It is merely asserted that unless orienting germs are excluded the interpretation of the appearance of the metastable modification may be quite different from that suggested by de Coppet[15] and others.

Going somewhat further afield it is not perhaps entirely fantastic to suggest that the large groups of molecules which are indicated by certain x-ray diffraction patterns in liquids may be due to a similar cause. If this were the case there would be no difficulty in reconciling the measurements of Stewart and Morrow[16] with the more recent results of Trillat.[17] While it is highly unlikely that an alcohol of a low molecular weight two hundred degrees above its melting point should contain germs bearing the crystalline adsorbate, it is perhaps worth while to exclude the possibility by preheating and distillation *in vacuo*. x-Ray diffraction offers, in fact, a most promis-

[15] L. C. de Coppet, *Ann. chim. phys.*, [5] **6**, 275 (1875); [8] **10**, 457 (1907).

[16] G. W. Stewart and R. M. Morrow, *Phys. Rev.*, **29**, 919 (1927).

[17] J. J. Trillat, *J. chim. phys.*, **27**, 525 (1930).

ing means of directly detecting the existence of the crystalline state above the melting point, and preliminary experiments with molybdenum targets have already been undertaken with inconclusive results. A copper target tube for this purpose is at present under construction at the Loomis Laboratory.

Finally, there is a possibility that, by suitable experiments, the heat of melting on the adsorbent necessary to give the thermodynamic theory of adsorption from solutions[18] quantitative significance, may become accessible. If this hope proves founded it will provide the most suitable means for demonstrating the general existence of this phenomenon, and supply as well quantitative data concerning adsorption heats.

## Summary

It is suggested that crystal form may persist above the melting temperature if an adsorbent is present for which the heat of binding of the crystalline adsorbate is greater than that of the liquid adsorbate. This hypothesis is seen to be successful in accounting for the behavior of undercooled liquids observed by previous investigators, and to supply a plausible explanation for further experiments. Since the liquid adsorbate is in part undercooled above the melting temperature, a mechanism is found for the enhancement of the ability of a liquid to crystallize by treatment above its crystallization temperature. It is inferred from experimental evidence that the development of the crystalline adsorbate must require a considerable activation energy.

A somewhat similar explanation has been found to apply to the behavior of two types of supersaturated solution, and the relation of the hypothesis to the Law of Stages is discussed.

Possible applications of this viewpoint to x-ray diffraction, the purification of materials, the treatment of glasses and alloys, and the thermodynamic theory of adsorption are briefly indicated.

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[18] W. Heine and M. Polanyi, *Z. physik. Chem.*, **132**, 385 (1928).

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

# QUANTITATIVE SEPARATIONS BY THE THERMAL DECOMPOSITION OF ANHYDROUS MIXTURES OF METAL SULFATES[1]

BY H. H. WILLARD AND R. D. FOWLER

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## Introduction

When heated to high temperatures, the metal sulfates are reversibly decomposed into sulfur trioxide and oxides. The decomposition may take place in one of several ways, depending on the particular metal. In some cases decomposition results directly in an oxide wherein the metal has the same valence as in the sulfate; other sulfates decompose in steps, a basic sulfate first being formed, which subsequently decomposes into the oxide; in the decomposition of other sulfates, the metal may be oxidized or reduced. The sulfates which have been studied may be classified as follows

| | | |
|---|---|---|
| Type 1 | $MSO_4 \rightleftharpoons MO + SO_3$ | $NiSO_4$, $CoSO_4$, $MgSO_4$ |
| Type 2 | $xMSO_4 \rightleftharpoons xMO \cdot SO_3 + (x-1)SO_3$ | $ZnSO_4$, $CuSO_4$, $CdSO_4$, $BeSO_4$ |
| Type 3 | $M_2(SO_4)_3 \rightleftharpoons M_2O_3 + 3SO_3$ | $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $Ga_2(SO_4)_3$ |
| Type 4 | $xM_2(SO_4)_3 \rightleftharpoons xM_2O_3 \cdot SO_3 + (x-1)SO_3$ | $Cr_2(SO_4)_3$ rare earth sulfates |
| Type 5 | $M(SO_4)_2 \rightleftharpoons MO_2 + 2SO_3$ | $Th(SO_4)_2$ |
| Type 6 | $4M(SO_4)_2 \rightleftharpoons 2M_2(SO_4)_3 + 2SO_3 + O_2$ | $Ce(SO_4)_2$ |
| Type 7 | $M_2(SO_4)_3 \rightleftharpoons 2MO_2 + 2SO_3 + SO_2$ | $Ce_2(SO_4)_3$ |
| Type 8 | $2MSO_4 \rightleftharpoons M_2O_3 + SO_3 + SO_2$ | $FeSO_4$ |
| Type 9 | $3MSO_4 \rightleftharpoons M_3O_4 + 2SO_3 + SO_2$ | $MnSO_4$ |
| Type 10 | $2M_2SO_4 \rightleftharpoons 4M + 2SO_3 + O_2$ | $Ag_2SO_4$ |
| Type 11 | $MSO_4 \cdot K_2SO_4 \rightleftharpoons K_2SO_4 + MO + SO_3$ | $MgSO_4 \cdot K_2SO_4$, $BeSO_3 \cdot K_2SO_4$ |

In each case there is also a second, simultaneous reaction, the reversible dissociation of $SO_3$ into $SO_2$ and $O_2$

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

Measurements of the dissociation pressures of the sulfates of the commoner elements have been made by Keppeler and d'Ans,[2] Wöhler, Plüddemann, and Wöhler,[3] and Marchal[4] and of some rare earth sulfates by Wöhler and Grünzweig.[5] The dissociation pressure curves of some of the commoner elements are given in Fig. 1. The curves for the rare earths are given in Reference 5. It will be seen from these curves, that the pressures for different sulfates at any given temperature vary considerably, depending on the nature of the metal.

[1] From a dissertation submitted by R. D. Fowler to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Keppeler and d'Ans, *Z. physik. Chem.*, **62**, 89 (1908).

[3] Wöhler, Plüddemann and Wöhler, *Ber.*, **31**, 703 (1908).

[4] Marchal, *J. chim. phys.*, **22**, 325, 412, 493, 559 (1912).

[5] Wöhler and Grünzweig, *Ber.*, **46**, 1726 (1913).

In the case of the double sulfates $MgSO_4 \cdot K_2SO_4$ and $BeSO_4 \cdot K_2SO_4$, the dissociation pressures are not those of $MgSO_4$ and $BeSO_4$ at the same temperatures, but are considerably lower. With mixtures of $ZnSO_4$ and $Fe_2(SO_4)_3$ the pressure is that of $Fe_2(SO_4)_3$, the less stable of the two. No other double salts or mixtures are reported in the literature as having been studied.

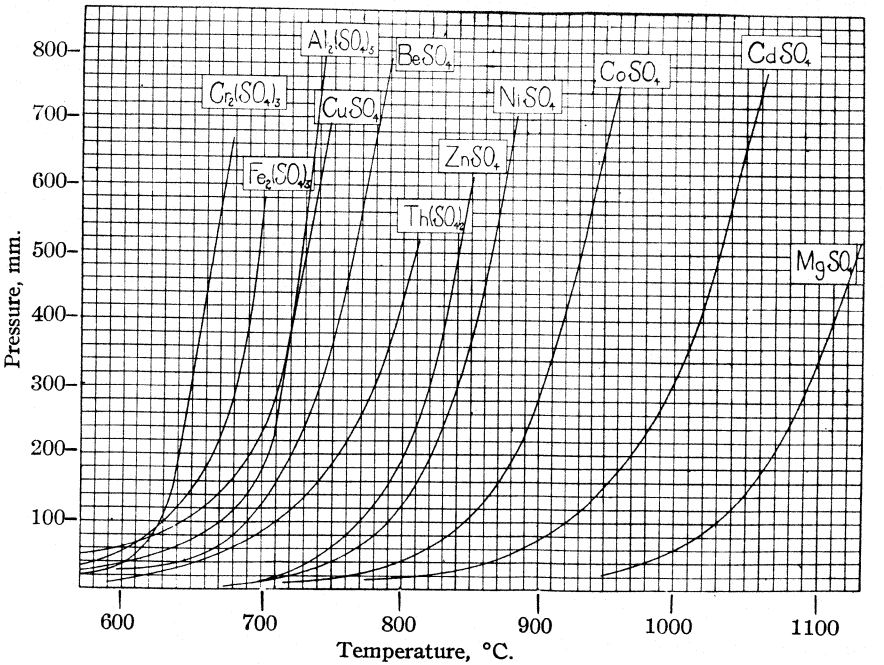


Fig. 1.—Dissociation pressures of some anhdyrous sulfates.

The solid decomposition product of any one of the sulfates listed is insoluble in water. Consequently, if a mixture of two sulfates were heated to some definite temperature, and the pressure of the gas phase maintained above the equilibrium pressure of the first sulfate, and below that of the second, the first would remain unaltered, while the second would form the insoluble product of decomposition. If the mixture could then be cooled before the reaction reversed appreciably, and then leached with water, the unaltered sulfate would be dissolved, thus removing it from the mixture. In this manner the otherwise very difficult separation of such elements as nickel and cobalt, beryllium and aluminum, hafnium and zirconium and particularly the metals of the rare earths, might be comparatively easily effected.

Both Wöhler and Grünzweig, and Mlle. Marchal call attention to the possibility of such separations; they considered them entirely feasible.

Wöhler and Grünzweig carried out the controlled decomposition of neodymium sulfate at such temperature and pressure that praseodymium sulfate placed next to it remained unchanged. They considered this a sufficient proof that separations were possible; no attempts at the actual separations of the mixtures have been described.

For the accomplishment of such separations, three factors are essential: (1) the sulfates must exert the same dissociation pressures in mixtures as they do individually; (2) the rate of the reverse reaction must be sufficiently slow to allow "quenching" of the equilibrium; and (3) the maintaining of the sulfates at high temperatures must not so change the physical state of the unaltered sulfate that its solution in water is made difficult.

The behavior of mixtures of sulfates on heating is of further interest, in connection with the study of solid solutions, which has been limited until comparatively recently to metals and a few chlorides. There have been several methods used in the study of solid solutions in metals such as the study of melting and freezing point diagrams, temperature–resistance curves, temperature–thermoelectric force curves, and determination of the crystal lattice constants from x-ray measurements. With solid solutions of salts, however, only the melting or freezing point method, and the use of x-rays, can be employed. Sulfate mixtures cannot, in general, be studied by the melting and freezing point method, since, for the most part, they decompose on heating, before melting. If two sulfates are miscible, it is very likely that their dissociation pressures will be considerably altered, and a study of their thermal decomposition at definite temperatures and pressures should be of interest in connection with the study of solid solutions.

The purpose of this research was to study the thermal decomposition of metal sulfates, with the objectives: (1) to determine the nature of the dissociation of, and (2) to ascertain the comparative structures of (*a*) mixtures of non-isomorphous sulfates, (*b*) mixtures of isomorphous sulfates; (*c*) double sulfates; (3) to determine the feasibility of the separation of elements by the controlled decomposition of mixtures of their anhydrous sulfates.

## Apparatus

The construction of the furnace used to decompose the sulfates at high temperatures is readily seen from Fig. 2. The major portion of the heat was supplied by a No. 16 B. and S. gage chromel ribbon a, 13 mm. in width, wound into a helix 48 mm. in diameter, with 3 mm. spacing between the turns. This was encased by an alundum tube b, 60 cm. long, having an internal diameter of 50 mm. and a wall thickness of 5 mm. The ends of the ribbon were bent at right angles to the axis of the helix, and brought out to heavy brass clamps, c, c′, through slots in the ends of the alundum tube.

To compensate for radiation loss at the ends of the furnace, coils d, d′, of No. 6 B. and S. gage chromel wire were wound around the outside of the alundum tube, 5 cm. from each end. Each coil consisted of seven turns, with 10 mm. spacing. The two

coils were connected in series, and the ends brought out through the furnace ends to the brass clamps e, e'.

A 25-cm. steel cylinder, A, 57 cm. long, formed the outer jacket of the furnace. Transite disks g, g', 16 mm. thick at each end of the jacket, served to support the alundum tube and heating coils so that their axes and the axis of the jacket were coincident. The space between the alundum tube and the inner wall of the jacket was filled with Filter-cel, which proved a satisfactory heat insulator. The furnace was horizontally suspended between parallel steel rods, which served as runners upon which to slide it into position over the reaction tube.

The main and end coils were heated separately by currents of 40–60 amperes at 10–15 volts, supplied through transformers. Since it was not practicable to adjust the heavy secondary currents by resistance variation, adjustment was made by varying the low current in the primary circuit, and as the currents in the main and end coils had to be adjusted independently, the use of two transformers was necessary.

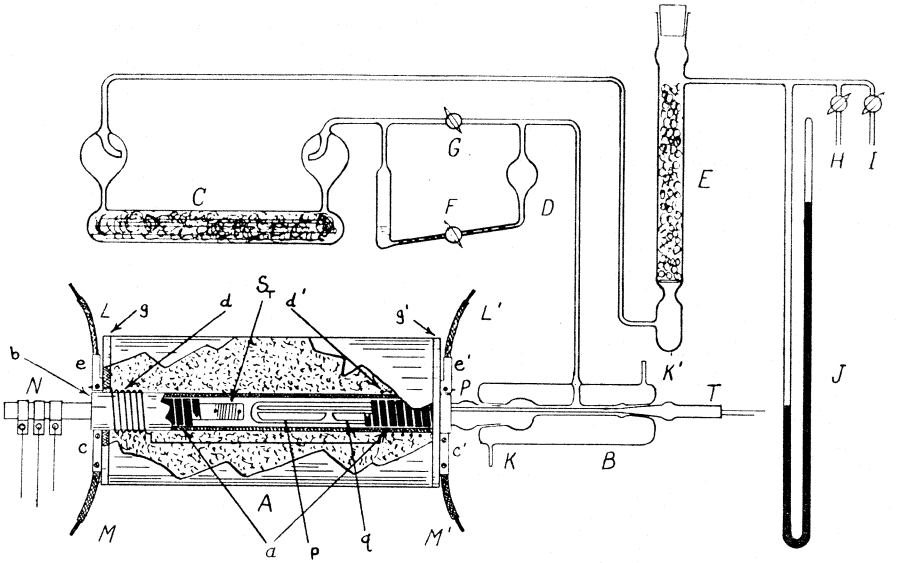


Fig. 2.—Apparatus for the controlled thermal decomposition of anhydrous metal sulfate mixtures.

The temperature of the furnace was automatically maintained constant, using the temperature variation in resistance of a small coil of fine platinum wire inside the furnace as a means of keeping the heating currents at definite average values. Reference to Fig. 3 will aid in the description of the operation. The platinum coil $S_T$ having a resistance of about 50 ohms at 1000°, together with the 50-ohm constantan resistances $S_1$ and $S_2$, and the variable constantan resistance $S_3$, form a Wheatstone bridge, to which current is supplied by the six-volt storage battery B. Resistance $S_3$ is set equal to the value that the thermostat coil $S_T$ is to have at the desired furnace temperature. If the furnace is at this temperature the Wheatstone bridge is balanced, and no current flows through the galvanometer G. When these conditions prevail, light falling from a source L, through a lens O, onto the galvanometer mirror, just misses being reflected to a focus on the photo-electric cell P. However, if the furnace temperature falls below the desired value, the resistance of $S_T$ decreases and the bridge becomes unbalanced. This

causes the reflection of the beam of light onto the photo-electric cell, bringing about a current flow through the latter. The photoelectric current is multiplied by the thermionic amplifier A to a value large enough to close the switch N, thereby decreasing the resistances in the primary circuits of the transformers $T_1$ and $T_2$. The IR drop across each primary is thus increased, with a consequent attendant increase in the secondary currents through the main coil M, and the end coils E, E′, resulting in a rise in the temperature of the furnace. When the desired temperature has again been reached, $S_T$ has a resistance equal to that of $S_3$, and the bridge is balanced, and the beam of light no longer falls on the photo-electric cell, allowing the switch N to open. The values of $R_1$ and $R_4$ are such that the secondary currents are now insufficient to maintain the furnace at the desired temperature, so that it again cools, repeating the cycle. In this manner, the temperature of the furnace fluctuates through a small interval, with the desired temperature as the average value.

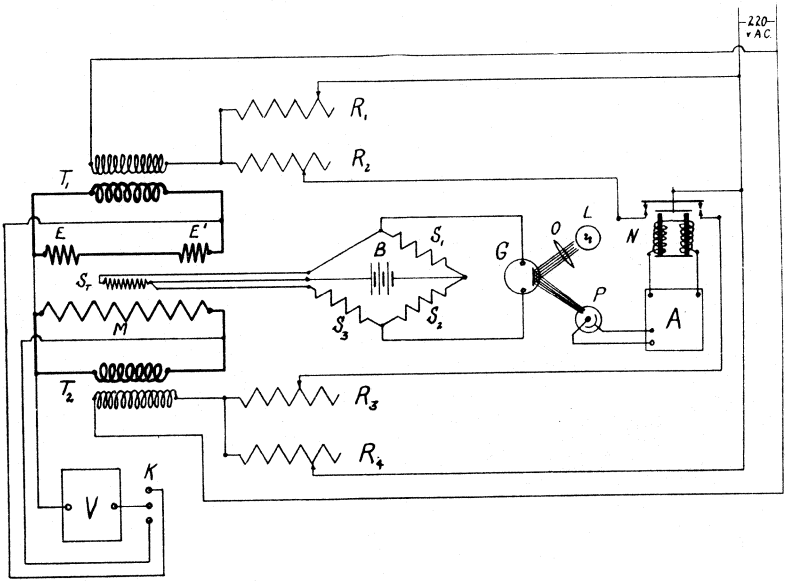


Fig. 3.—Circuit for furnace control.

The IR drop across the heating coils was measured with the voltmeter V, which could be thrown across the desired coil by means of the switch K. In this way the optimum secondary voltages of $T_1$ and $T_2$ were determined for a series of temperatures at 50-degree intervals, over the range to 1050°, thus allowing the furnace to be subsequently maintained at any desired temperature within this range with the minimum expenditure of time and labor. Thus, if it were desired to maintain the furnace at 1000°, $R_3$ and $R_4$ were so adjusted that the IR drop across the main heating coil fluctuated between 9 and 13 volts, while $R_1$ and $R_2$ were given such values that the potential across the end coils varied between 8.5 and 11.5 volts. $R_1$ and $R_4$ each consisted of two series-connected, 37-ohm, water-cooled rheostats, and $R_2$ and $R_3$ were single 37-ohm rheostats of the same type.

The galvanometer G was a Leeds and Northrup Type R, having a sensitivity of 250 megohms.

The photo-electric cell was of the potassium hydride type, and was illuminated

by a 27-candle-power, 6-volt lamp. Under the conditions of the present arrangement, full illumination of the photo-electric cell produced a current of about $3 \times 10^{-7}$ amperes, when a potential of 112.5 volts was applied to it. This small current was boosted by thermionic amplification to about 30 milli-amperes, which nicely operated the switch changing the furnace current. The amplifier circuit is shown in Fig. 4. As the principles and applications of thermionic amplification have been thoroughly discussed by Van der Bijl,[6] Morecroft,[7] Nottingham,[8] and others, the circuit will not be described here.

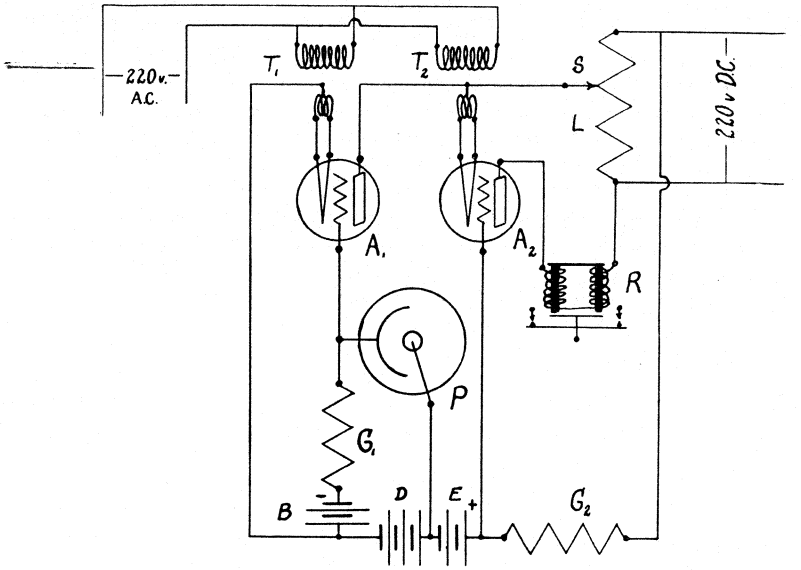


Fig. 4.—Amplifier circuit: $A_1$ and $A_2$, Western Electric 216A power amplifiers; $T_1$ and $T_2$, 220 to 5.5 volt transformers; P, photo-electric cell; $G_1$, 15 megohm grid leak; $G_2$, 0.1 megohm grid leak; B, 45-volt battery; D, 67.5-volt battery; E, 112.5-volt battery; L, 1400-ohm slide wire rheostat; R, 2600-ohm magnetic switch.

In connecting the platinum resistance $S_T$ to the other arms of the Wheatstone bridge, the three lead method of Siemens[9] was used to compensate for any variation in the resistance of the flexible copper wire leads that might be brought about by changes in the temperature of the room.

This thermostat served to maintain the furnace constant to within 0.1°, for as long as twenty-four hours. By properly supplementing the heat supplied by the main furnace coil with that from the end coils, the temperature could be maintained uniform to within 1°, over a central portion of the furnace extending to about 10 cm. from each end.

[6] Van der Bijl, "The Thermionic Vacuum Tube," McGraw-Hill Book Co., Inc., New York, 1920.

[7] Morecroft, "Principles of Radio Communication," John Wiley and Sons, Inc., New York, 1921.

[8] Nottingham, *J. Franklin Instit.*, **208**, 469 (1929); **209**, 287 (1930).

[9] Burgess and le Chatelier, "The Measurement of High Temperatures," John Wiley and Sons, Inc., New York, 1912.

**Temperature Measurement.**—Temperature measurement was made by a platinum–platinum-rhodium thermocouple, placed inside the reaction chamber. The cold junction was immersed in a mixture of ice and water in a Dewar flask. A Leeds and Northrup thermocouple potentiometer and a Leeds and Northrup Type R galvanometer having a sensitivity of 250 megohms were used in conjunction with the thermocouple. The Holman formula

$$\log e = n \log t + \log m$$

was used to convert the e. m. f. values of the thermocouple to temperatures (see reference 9, page 112). Temperatures of fixed points determined by using this formula have a maximum departure of −2.5° from the gas thermometer scale values. The values of the temperature and pressure of sulfur trioxide were so chosen for each pair of sulfates that such a departure would have no effect. In the case of the sulfates of praseodymium and neodymium, where the difference in dissociation pressures is the smallest of all the pairs studied, the pressures of sulfur trioxide at 1015° are, respectively, 715 and 780 mm., and at 1017.5°, 740 and 810 mm. Consequently, a positive error of 2.5° in setting the temperature is just permissible. With all the other sulfate pairs, a greater error is permissible. To determine the constants $n$ and $m$, the e. m. f.'s of the thermocouple were measured at the sulfur boiling point, and at the melting point of gold, the latter point being obtained by the wire method (reference 9, page 183–185). At 1000°, the thermoelectric power, $dE/dt$, of the thermocouple was 11.5 microvolts per degree, consequently a change of temperature of 0.1° would produce an e. m. f. change of 1.15 microvolts, which is well within the sensitivity of the potentiometer. It is probable that the control apparatus could be eliminated by the use of a source of power of constant voltage, such as would be obtained by the use of a suitable voltage regulator, or from a generator driven by a synchronous motor.

**Decomposition Chamber and Constant Pressure System.**—The arrangement of the decomposition apparatus is shown in Fig. 2. The sulfate mixture to be investigated was placed in a porcelain boat p, in the quartz tube P. This quartz tube was ground into the Pyrex jacket B, through which water at 70–80° was circulated, by means of an electric heater and reservoir forming a closed hydraulic circuit through connections at K and K′. The thermocouple was encased in a quartz tube T, ground into the other end of the jacket. This jacket served to keep the ground joints cool and, simultaneously, to prevent the condensation of sulfur trioxide. A T-connection led from the interior through the side of the jacket, to the phosphoric acid by-pass D, which was connected in turn to the manometer J, through the sulfur trioxide absorbers C and E. C was packed with glass wool and half-filled with 70% sulfuric acid, and E contained soda-lime. The manometer J was of the closed tube type, one meter long, and was made from tubing having a bore of 10 mm. A wooden scale with millimeter divisions was used to set the height of the mercury column. The system could be evacuated to 4–5 mm. by a Cenco pump, through stopcock H, and filled with air to any desired pressure through stopcock I.

The tube leading from the jacket B to the by-pass D, the by-pass itself, and the tube connecting it to the sulfuric acid chamber C, were maintained at about 100° by an electrically heated winding of Chromel wire, to prevent the condensation of sulfur trioxide. The quartz-to-pyrex joints and the stopcocks F and G were lubricated with a stiff, clear paste made by dissolving phosphorus pentoxide in 85% phosphoric acid at 110°. All other stopcocks were lubricated with a grease made from white vaseline and pure rubber. The general arrangement of the apparatus is best seen from Fig. 2 and the details of the decomposition chamber and water jacket from Fig. 5.

**Method of Procedure.**—In effecting a controlled decomposition, the sulfate mixture was placed in a porcelain boat p, and anhydrous ferric sulfate placed in another boat q,

in the reaction tube, and the latter joined to the Pyrex jacket. After placing the thermocouple in position, stopcock G was opened, F and I closed, and the system evacuated through H. When the pressure had been reduced to 4–5 mm., H and G were closed, and air admitted through I, to the desired pressure. The ferric sulfate was now decomposed by heating that portion of the quartz tube immediately surrounding it with a blow torch. Stopcock F was opened from time to time to determine when the pressure of sulfur trioxide exceeded the desired value, by noting the direction of movement of the phosphoric acid thread in the by-pass D. As soon as sulfur trioxide started to bubble through the by-pass to the absorbers C and E, stopcock F was left open, and the furnace, which had previously been brought to the desired temperature, moved into

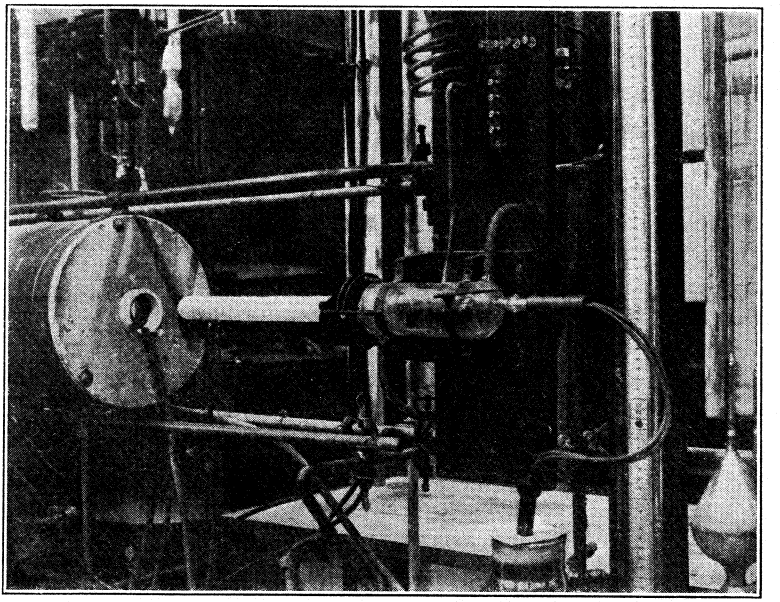

Fig. 5.—Detail of decomposition chamber.

such a position over the quartz tube that the decomposition of the ferric sulfate (as well as the sulfates being investigated) proceeded slowly for about three-quarters of an hour. This procedure was found necessary to allow the phosphoric acid in the lubricant, and in the by-pass, to become saturated with sulfur trioxide. After three-quarters of an hour, the furnace was moved completely over the reaction tube, and the reactions allowed to proceed to completion, as indicated by cessation of the bubbling of sulfur trioxide through the by-pass. This required from two to ten hours, depending on the amount of sulfate mixture, and the decomposition temperature.

During the progress of a decomposition it was occasionally necessary t o reset the air pressure, since the recombination of the equilibrium mixture of sulfur dioxide and oxygen to sulfur trioxide was not complete, leaving some oxygen which was not taken up by the absorbers C and E.

Upon completion of a decomposition, stopcock F was closed, the furnace moved out of position, and the reaction tube was immediately quenched with cold water, then again evacuated, by opening H and G in succession, and then filled with air by closing H and

opening I, after which it was detached from the water jacket, and the boat with the decomposed mixture removed to a desiccator. Due to the thinning out of the phosphoric acid lubricant on the joint between the quartz tube and the water jacket, the two became very firmly stuck together, so that a special screw wedge had to be employed to effect their separation. This may be seen in position in Figure 5. It proved to be very efficacious, and neither the quartz tube nor the water jacket was ever damaged, although at times after the many runs for which they were used, it would have been utterly impossible to get them apart by any other means. No trouble was ever caused by sticking of the very much smaller joint between the thermocouple and the water jacket.

**Spectrographic Equipment.**—Since none of the rare earths except cerium,[10] europium[11] and ytterbium[12] can be determined analytically when present in mixtures with other rare earths, three methods were available for studying the decomposition products of mixed rare earth sulfates: (1) determination of the mean equivalent weight; (2) measurement of the magnetic susceptibility; (3) observation of the emission and absorption spectra.

Of these methods, (1) is of no value when the elements constituting a mixture have atomic weights lying close together; (2) is of value only when the susceptibilities of the elements are considerably different, and (3) can only serve to ascertain with certainty the presence or absence of a particular element in a mixture, although it may afford an approximate idea as to the composition.

The rare earths available for this work were the ceria earths, cerium, neodymium, praseodymium, samarium and lanthanum. As has been mentioned, cerium can be determined analytically. The atomic weights of the other ceria earths are: La, 138.9; Pr, 140.9; Nd, 144.3; and Sm, 150.4. Consequently the determination of the mean equivalent weight of a mixture is of little significance, except possibly in the case of a mixture of samarium with one of the other ceria earths.

The susceptibilities of the ceria earth sulfate octahydrates, expressed in C. G. S. units, are as follows[13]

| La | $Ce^{III}$ | Pr | Nd | Sm |
|---|---|---|---|---|
| −00.84 | +22.0 | +51.0 | +52.0 | +12.0 |

These values are hardly far enough apart to make the determination of magnetic susceptibility a satisfactory means of analysis.

The comparison of the spectra of the soluble and insoluble products of decomposition with those of the original mixtures was therefore the only reliable means of analysis in studying the decomposition of rare earth sulfate mixtures.

[10] Willard and Young, THIS JOURNAL, **50**, 1379 (1928); Furman and Wallace, *ibid.*, **51**, 1449 (1929).

[11] Yntema, *ibid.*, **52**, 2782 (1930).

[12] Ball and Yntema, *ibid.*, **52**, 4264 (1930).

[13] Decker, *Ann. Physik*, **79**, 324 (1926).

Two spectrographs were available, a small Zeiss glass prism instrument, and a Hilger E-316 quartz spectrograph. The range of the former was 3800 to 8000, and the latter, 2000 to 10,000 Ångström units.

The Zeiss spectrograph was used mainly for absorption spectra in the visible region, with mixtures containing neodymium or praseodymium. The solutions studied were contained in a Baly absorption tube, using a tungsten arc (Point-O-Lite) as a light source.

The arc spectra of the rare earth mixtures were studied with the Hilger spectrograph, using a 6-ampere arc between pure Acheson graphite electrodes.

Quantitative spectrum analysis of rare earth mixtures has been recently described by Quill, Selwood and Hopkins[14] and by Selwood.[15]

**x-Ray Apparatus.**—The crystal structure of the sulfate mixtures was studied by the Hull–Debye–Scherrer powder method of x-ray diffraction, using a General Electric apparatus.[16] Since the method and apparatus involved have been very completely described by Davey,[17] no description is necessary here.

As the diffraction lines obtained by the powder method are rather broad, it was deemed advisable to determine the position of maximum intensity for each line by the use of a Zeiss microphotometer.

**Materials.**—The sulfates of iron, zinc, beryllium, aluminum, magnesium, nickel and cobalt were of the best quality obtainable from commercial supply houses. The following rare earth salts were kindly supplied by Dr. H. S. Miner of the Welsbach Company: $Ce_2(SO_4)_3 \cdot 8H_2O$, $La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$, $Pr(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$, $Nd(NO_3)_3 \cdot 10H_2O$, $Sm_2(C_2O_4)_3 \cdot 10H_2O$.

For spectroscopic comparison, the following very pure rare earth oxides were obtained from Adam Hilger, Ltd., London: $La_2O_3$, $Sm_2O_3$, $PrO_2$-$Pr_2O_3$, $Nd_2O_3$.

**Thermal Decompositions.**—Series 1 to 6. Mixtures of non-isomorphous sulfates, and mixtures of cerous sulfate with some other rare-earth sulfates. Anhydrous ferric, aluminum, zinc and beryllium sulfates were prepared from the C. P. hydrated sulfates by heating to constant weight at 400–450°. Anhydrous cerous sulfate was prepared by dehydrating the octahydrate at 600–650°. Anhydrous lanthanum, praseodymium, and neodymium sulfates were prepared from the double ammonium nitrates by evaporation of the latter to dryness with sulfuric acid, and heating of the

[14] Quill, Selwood and Hopkins, THIS JOURNAL, **50**, 2929 (1928).

[15] Selwood, *Ind. Eng. Chem., Anal. Ed.*, **2**, 93 (1930).

[16] The use of the apparatus was very kindly extended to the authors by Mr. Sherman Gerhard of the Physics Department, to whom appreciation is expressed.

[17] Davey, (a) *J. Optical Soc. Am.*, **5**, 479 (1921); (b) *Gen. Elec. Rev.*, **25**, No. 9, 565 (1922).

residues to constant weight at 600–650°. Portions of the anhydrous cerous and lanthanum sulfates were then dissolved separately in cold water, and the cerium oxidized with persulfate in the presence of silver nitrate, according to the method of Willard and Young.[18]

After destroying the excess of persulfate by boiling, the ceric sulfate was titrated with freshly standardized hydrogen peroxide according to the method of Furman and Wallace[19] with the following results: $Ce_2(SO_4)_3$, 98.49% pure; $La_2(SO_4)_3$ contained 1.82% $Ce_2(SO_4)_3$. The praseodymium and neodymium sulfates were found to be free from cerium.

Pairs of the anhydrous sulfates were then mixed in the desired proportions, dissolved in 1:5 sulfuric acid, evaporated to dryness and heated to constant weight at 400–450° for those pairs containing iron, zinc, beryllium or aluminum, and at 600–650° for those containing the rare earths. Some of the mixture in each case was then weighed into a small porcelain or quartz boat, which was then placed in a larger boat, and introduced into the decomposition chamber in the manner previously outlined. To prevent the absorption of moisture, weighings were made by placing the crucibles containing the anhydrous sulfates in ordinary weighing bottles, and the boats in specially constructed bottles provided with legs, using a similar empty weighing bottle as a counterpoise.

The reaction tube contained not only the mixed sulfates, but also another boat containing about 10 g. of anhydrous ferric sulfate, and the decomposition was carried out as previously described. The heating was continued until sulfur trioxide ceased to bubble through the phosphoric acid by-pass, and then for one hour more (that is, for six hours unless otherwise noted), after which the sulfates were removed to a desiccator in the manner previously described. After it had been weighed, the decomposed mixture was treated with water, and the insoluble portion filtered off. This was either ignited directly to oxide and weighed, or converted to anhydrous sulfate and then weighed or analyzed, while the soluble portion was either precipitated as hydroxide by sodium carbonate and ignited to oxide and weighed, or else evaporated to dryness, dehydrated, and weighed as anhydrous sulfate. The results are given in Series 1 to 6.

From these results the conclusion was reached that the anhydrous sulfate pairs, $Zn–Fe^{III}$, Zn–Al, Be–Al, Ce–La, Ce–Pr and Ce–Nd may be separated into their constituents by controlled decomposition. The first three pairs are made up of non-isomorphous sulfates; solid solutions do not appear to be formed in these cases. x-Ray diffraction photographs taken by the Hull–Debye–Scherrer method on the Be–Al sulfate mixture confirm these conclusions, no evidence of solid solution formation being shown, as the lines occurring in the individual spectra of the pure sulfates appear

[18] Willard and Young, THIS JOURNAL, **50**, 1379 (1928).

[19] Furman and Wallace, *ibid.*, **51**, 1449 (1929).

Series 1. $Fe_2(SO_4)_3$–$ZnSO_4$

Temperature, 800°. Dissociation pressure of $Fe_2(SO_4)_3$ >2 atm.
Pressure, 740 mm. Dissociation pressure of $ZnSO_4$, 195 mm.[4]

| | Run a, g. | Run b, g. |
|---|---|---|
| Composition of mixture { $Fe_2(SO_4)_3$ | 2.0015 | 1.1250 |
| Composition of mixture { $ZnSO_4$ | 2.3123 | 2.4356 |
| Weight mixture taken | 2.3149 | 2.4356 |
| Weight $SO_3$ lost | 0.6440 | 0.4616 |
| Theoretical $SO_3$ loss from $Fe_2(SO_4)_3$ forming $Fe_2O_3$ | .6451 | .4626 |
| Weight $Fe_2O_3$ found | .4280 | .3068 |
| Weight $Fe_2O_3$ calculated | .4289 | .3075 |
| Weight ZnO found | .6272 | .8419 |
| Weight ZnO calculated | .6255 | .8405 |

Series 2. $Al_2(SO_4)_3$–$ZnSO_4$

Temperature, 800°. Dissociation pressure of $Al_2(SO_4)_3$ >2 atm.
Pressure, 740 mm. Dissociation pressure of $ZnSO_4$, 195 mm.[4]

| | Run a, g. | Run b, g. |
|---|---|---|
| Composition of mixture { $Al_2(SO_4)_3$ | 2.3146 | 1.2981 |
| Composition of mixture { $ZnSO_4$ | 2.2220 | 2.5673 |
| Weight of mixture taken | 2.4563 | 2.5602 |
| Weight $SO_3$ lost | 0.8788 | 0.6029 |
| Theoretical $SO_3$ loss from $Al_2(SO_4)_3$ forming $Al_2O_3$ | .8796 | .6036 |
| Weight $Al_2O_3$ found | .3726 | .2556 |
| Weight $Al_2O_3$ calculated | .3733 | .2562 |
| Weight ZnO found | .6086 | .8588 |
| Weight ZnO calculated | .6065 | .8572 |

Series 3. $BeSO_4$–$Al_2(SO_4)_3$

Temperature, 750°. Dissociation pressure of $BeSO_4$, 365 mm.
Pressure, 740 mm. Dissociation pressure of $Al_2(SO_4)_3$, 900 mm.[4]

| | Run a, g. | Run b, g. |
|---|---|---|
| Composition of mixture { $BeSO_4$ | 1.5768 | 1.0559 |
| Composition of mixture { $Al_2(SO_4)_3$ | 1.7632 | 2.3178 |
| Weight of mixture taken | 2.5764 | 2.8377 |
| Actual $SO_3$ loss | 0.9540 | 1.3675 |
| Theoretical $SO_3$ loss, from $Al_2(SO_4)_3$ forming $Al_2O_3$ | .9548 | 1.3686 |
| Weight soluble portion as anhydrous sulfate | 1.2175 | 0.8898 |
| Weight $BeSO_4$ taken | 1.2163 | .8882 |
| Weight insoluble portion as $Al_2O_3$ | 0.4048 | .5803 |
| Weight $Al_2(SO_4)_3$ found | 1.3586 | 1.9476 |
| Weight $Al_2(SO_4)_3$ taken | 1.3601 | 1.9495 |

Series 4. $Ce_2(SO_4)_3$–$La_2(SO_4)_3$

Temperature, 920°. Dissociation pressure of $Ce_2(SO_4)_3$, 850 mm.
Pressure, 740 mm. Dissociation pressure of $La_2(SO_4)_3$, 70 mm.[5]

| | Run a, g. | Run b, g. |
|---|---|---|
| Composition of mixture { $Ce_2(SO_4)_3$ | 1.2134 | 1.3162 |
| Composition of mixture { $La_2(SO_4)_3$ | 1.1103 | 0.7263 |
| Weight mixture taken | 2.3140 | 2.0115 |
| Actual ($SO_2$ + $SO_3$) loss | 0.4767 | 0.5079 |
| Theoretical ($SO_2$ + $SO_3$) loss | .4771 | .5084 |
| Weight of insoluble portion as sulfate | 1.2099 | 1.2890 |
| Weight $Ce_2(SO_4)_3$ found by titration in insoluble portion | 1.2095 | 1.2885 |
| Weight $Ce_2(SO_4)_3$ taken | 1.2102 | 1.2897 |

Series 5. $Ce_2(SO_4)_3$–$Pr_2(SO_4)_3$

Temperature, 920°. Dissociation pressure of $Pr_2(SO_4)_3$, 145 mm.[5]
Pressure, 740 mm.

| | Run a, g. | Run b, g. |
|---|---|---|
| Composition of mixture { $Ce_2(SO_4)_3$ | 0.5326 | 0.7896 |
| Composition of mixture { $Pr_2(SO_4)_3$ | .5116 | .4317 |
| Weight mixture taken | 1.0237 | 1.1987 |
| Actual ($SO_2$ + $SO_3$) loss | 0.2025 | 0.3004 |
| Theoretical ($SO_2$ + $SO_3$) loss | .2027 | .3009 |
| Weight of insoluble portion as sulfate | .5139 | .7627 |
| Weight $Ce_2(SO_4)_3$ found by titration in insoluble portion | .5139 | .7624 |
| Weight $Ce_2(SO_4)_3$ taken | .5143 | .7633 |

Series 6. $Ce_2(SO_4)_3$–$Nd_2(SO_4)_3$

Temperature, 920°. Dissociation pressure of $Nd_2(SO_4)_3$, 170 mm.[5]
Pressure, 740 mm.

| | Run a, g. | Run b, g. |
|---|---|---|
| Composition of mixture { $Ce_2(SO_4)_3$ | 0.5116 | 0.6321 |
| Composition of mixture { $Nd_2(SO_4)_3$ | .4998 | .3872 |
| Weight mixture taken | .9992 | .9976 |
| Actual ($SO_2$ + $SO_3$) loss | .1958 | .2395 |
| Theoretical ($SO_2$ + $SO_3$) loss | .1962 | .2402 |
| Weight of insoluble portion as sulfate | .4972 | .6087 |
| Weight $Ce_2(SO_4)_3$ found by titration in insoluble portion | .4969 | .6082 |
| Weight $Ce_2(SO_4)_3$ taken | .4978 | .6093 |

without shift in the spectra of the mixture. This is evident from Fig. 6, particularly from the photometer curves.

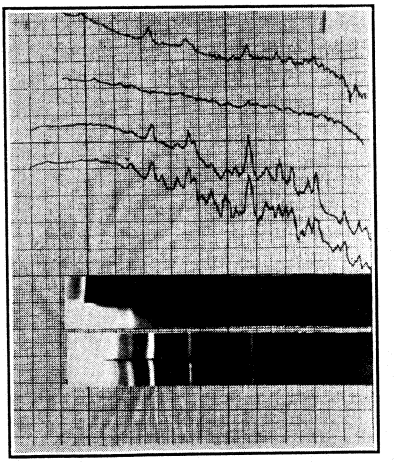


Fig. 6.—x-Ray spectra and photometer curves of beryllium and aluminum sulfates.

Cerous sulfate is isomorphous with the other rare earth sulfates, but thermal decomposition results in $CeO_2$, which is not isomorphous with the rare earth sesquioxides; as the results show, separation of cerium from the other rare earths by controlled thermal decomposition is therefore possible.

Series 7 to 12. Mixtures of isomorphous sulfates, including some rare earth sulfate mixtures not containing cerium. Anhydrous sulfates of nickel, cobalt and magnesium were prepared from the C. P. hydrated sulfates by heating to constant weight at 500–650°, the lower temperature being necessary for nickel. Pairs of these and pairs of the anhydrous sulfates of lanthanum, praseodymium and neodymium were then mixed, dissolved in water, dehydrated and decomposed in a manner exactly analogous to that of Series 1 to 6. In addition to the mixed sulfates, the pure sulfate constituents of each pair were placed simultaneously in the decomposition chamber, in separate adjacent boats. The results are shown in Series 7 to 12.

**Series 7.** $BeSO_4$–$ZnSO_4$.—Temperature, 800°. Pressure, 740 mm. Dissociation pressure of $BeSO_4$, 950 mm.; of $ZnSO_4$, 195 mm. 2.0132 g. of pure $BeSO_4$ lost 1.2263 g. of $SO_3$, forming $5BeO \cdot SO_3$; theoretical loss, 1.2272 g. The residue was boiled for thirty minutes with water. After filtering off the residue, ammonia produced in the filtrate only a slight turbidity, indicating complete decomposition of the $BeSO_4$. 2.3216 g. of pure $ZnSO_4$ lost 0.0013 g.; theoretically there should have been no loss. Hot water dissolved all but a trace of it.

The mixture consisted of 2.6512 g. of $ZnSO_4$ and 2.1314 g. of $BeSO_4$. Of this mixture, 2.1206 g. lost 0.6561 g. of $SO_3$ as compared to a theoretical of 0.5760 if only $BeSO_4$ decomposed. The weight of the insoluble portion, converted into anhydrous sulfates, was 1.2828 g. The beryllium in this was precipitated as $Be(OH)_2$ by ammonia and yielded 0.1649 g. of BeO, corresponding to 0.6925 g. of $BeSO_4$ and leaving 0.5903 g. of $ZnSO_4$. The original mixture contained 44.57% of $BeSO_4$ and the decomposed portion, 53.98%.

**Series 8.** $BeSO_4$–$MgSO_4$.—Temperature, 1000°. Pressure, 740 mm. Dissociation pressure of $BeSO_4 > 2$ atm.; of $MgSO_4$, 60 mm.[4] 2.5316 g. of pure $BeSO_4$ lost 1.5432 g. of $SO_3$, forming $5BeO \cdot SO_3$; theoretical loss 1.5430 g. The residue was tested as above with the same results. 3.1579 g. of pure $MgSO_4$ lost 0.0003 g., or practically no loss, and hot water dissolved all but a trace of it.

The mixture consisted of 1.5632 g. of $BeSO_4$ and 1.5226 g. of $MgSO_4$. Of this, 2.5350 g. lost 0.7685 g. of $SO_3$ instead of the theoretical 0.7827 g. The insoluble portion as anhydrous sulfates weighed 1.3345 g. and contained 0.7551 g. of $BeSO_4$, leaving 0.5794 g. of $MgSO_4$. The original mixture contained 50.66% of $BeSO_4$ and the decomposed portion, 56.58%.

**Series 9.** $NiSO_4$–$CoSO_4$.—Temperature, 920°. Pressure, 740 mm. Dissociation pressure of $NiSO_4$, 1400 mm.; of $CoSO_4$, 420 mm.[4] 2.6882 g. of $NiSO_4$ lost 1.3910 g. of $SO_3$, instead of the theoretical 1.3908, g. to form NiO. It was completely insoluble in water. 3.7645 g. of $CoSO_4$ lost 0.0003 g. or practically nothing, and all but a trace of it was soluble in water.

The mixture consisted of 2.5031 g. of $NiSO_4$ and 2.6345 g. of $CoSO_4$. Of this, 2.7543 g. lost 0.8290 g. instead of the theoretical 0.6943 g. The residue was extracted with hot water, and the insoluble portion, treated with sulfuric acid and heated to constant weight at 500–550° yielded 1.6022 g. of anhydrous sulfates. The nickel in this was determined by double precipitation with dimethylglyoxime. The cobalt was determined by difference. The same method was used for the soluble portion. In the insoluble portion, weighing, as sulfates, 1.6022 g., the weight of $NiSO_4$ was 1.0193 g. and the $CoSO_4$, 0.5829 g. The soluble portion, by difference, amounted to 1.1521 g. and consisted of 0.3226 g. of $NiSO_4$ and 0.8295 g. of $CoSO_4$. Thus the $NiSO_4$ constituted 48.72% of the original mixture, 62.17% of the insoluble residue and 28.00% of the soluble portion.

The x-ray diffraction photographs and their photometer curves in Fig. 7 show very clearly evidence of formation of solid solutions. There is a distinct shift of the lines in the crystallized mixture as compared with those for the pure substances or in a mechanical mixture.

**Series 10.** $Nd_2(SO_4)_3$–$La_2(SO_4)_3$.—Temperature, 1020°. Pressure 740 mm. Dissociation pressure of $Nd_2(SO_4)_3$, 840 mm.; of $La_2(SO_4)_3$, 370 mm. In run A, 0.5982 g. of pure $Nd_2(SO_4)_3$ lost 0.1650 g. of $SO_3$, forming $Nd_2O_3 \cdot SO_3$; theoretical loss, 0.1660 g. Only a few tenths of a mg. dissolved in water. 0.6147 g. of pure $La_2(SO_4)_3$ lost 0.0047 g., due to the impurity of $Ce_2(SO_4)_3$, which should have lost 0.0044 g.; all but a trace dissolved. The mixture consisted of 0.4322 g. of $Nd_2(SO_4)_3$ and 0.4418 g. of $La_2(SO_4)_3$. 0.8613 g. of this lost 0.0479 g. instead of the theoretical 0.1213 g. The decomposed mixture was then treated with water. The undecomposed portion of the mixture was dissolved, the residue filtered off, converted to anhydrous sulfate by evaporation with concentrated sulfuric acid and heated at 600° to constant weight. This resulted in 0.1722 g. of anhydrous sulfate mixture.

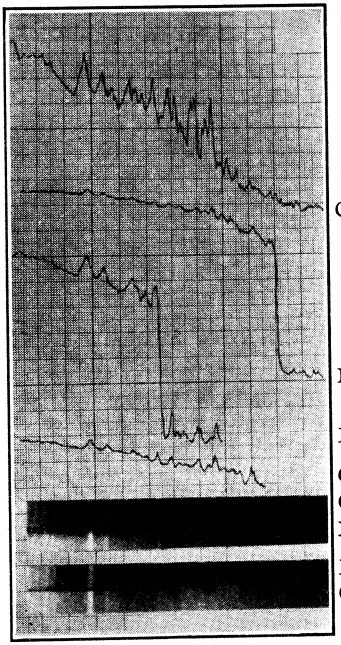


Fig. 7.—x-Ray spectra and photometer curves of cobalt and nickel sulfates.

The approximate composition of the decomposed portion of the sulfate mixture was calculated from its weight and the total loss of sulfur trioxide as being 0.155 g. $Nd_2(SO_4)_3$, 0.017 g. $La_2(SO_4)_3$.

A qualitative confirmation of the fractionation was obtained by photographing the arc spectra of the soluble and insoluble portions. It is evident that the apparent fractionation of the neodymium-lanthanum sulfate mixture is due only to the fractionation obtained in crystallization: that is, all crystals deposited previous to a certain point in the process of crystallization will have such a composition that their decomposition pressures will be less than the pressure of sulfur trioxide arbitrarily maintained in the reaction chamber, while all those subsequently deposited will be sufficiently rich in neodymium sulfate so that their decomposition pressures will exceed this pressure.

**Run (B).—To confirm the conclusions drawn from Run (A) the following experiment was performed.**

The two fractions obtained in Run (A) were dissolved together in water, and the solution placed in a 100-cc. graduated cylinder, which was then immersed in a beaker of oil, on a hot-plate. When crystals just started to appear, the volume of the solution was noted, and the evaporation continued until the volume had decreased to one-fifth of the value noted. The remaining solution was then quickly decanted from the crystals

(which we may designate A) into a small beaker, and the evaporation continued in this, to dryness, resulting in a second portion of crystals, B. Crystals A with adhering solution were transferred to a small beaker, and evaporated to dryness. The two crystalline masses were then heated to constant weight at 600°, and placed in separate adjacent boats in the reaction chamber. The pressure of sulfur trioxide and the temperature were set to the values used in Run (A). After four hours' heating, the boats were removed from the furnace, cooled, and their contents treated with water. Practically all of the crystals A dissolved, while only a very small part of the crystals B went into solution. The arc spectra of A and B showed B to be richer in neodymium than A.

**Series 11.** $Pr_2(SO_4)_3$–$La_2(SO_4)_3$.—Temperature, 1030°. Pressure, 740 mm. Dissociation pressure of $Pr_2(SO_4)_3$, 865 mm.; of $La_2(SO_4)_3$, 430 mm. 0.5774 g. of pure $Pr_2(SO_4)_3$ lost 0.1615 g. of $SO_3$, forming $Pr_2O_3 \cdot SO_3$; theoretical loss, 0.1622. It was practically insoluble in water. 0.6744 g. of pure $La_2(SO_4)_3$ lost 0.0050 g. due to the impurity of $Ce_2(SO_4)_3$, which required 0.0048 g. All but a very small amount dissolved in water.

The mixture consisted of 0.3216 g. of $Pr_2(SO_4)_3$ and 0.3114 g. of $La_2(SO_4)_3$. Of this mixture, 0.6312 g. lost 0.0344 g. of $SO_3$, instead of the theoretical 0.0923 g. The insoluble portion was filtered off and converted into anhydrous sulfates weighing 0.1222 g. From this weight and the loss in $SO_3$ the composition of the insoluble portion was calculated to be 0.106 g. of $Pr_2(SO_4)_3$ and 0.016 g. of $La_2(SO_4)_3$.

**Series 12.** $Nd_2(SO_4)_3$–$Pr_2(SO_4)_3$.—Temperature, 1015°. Pressure, 740 mm. Dissociation pressure of $Nd_2(SO_4)_3$, 780 mm.; of $Pr_2(SO_4)_3$, 715 mm. 0.5549 g. of pure $Nd_2(SO_4)_3$ lost 0.1553 g. of $SO_3$, forming $Nd_2O_3.SO_3$; theoretical loss, 0.1562 g. It was practically insoluble in water. 0.6117 g. of $Pr_2(SO_4)_3$ lost 0.0003 g. or practically nothing; all but a trace dissolved in water.

The mixture consisted of 0.3227 g. of $Nd_2(SO_4)_3$ and 0.3009 g. of $Pr_2(SO_4)_3$. Of this, 0.6125 g. lost 0.0041 g., instead of the theoretical 0.0892 g., and all but about 0.01 g. dissolved in water.

**Series 13.** $BeSO_4$–$K_2SO_4$.—The double sulfate $BeSO_4 \cdot K_2SO_4 \cdot 2H_2O$ was prepared by dissolving equimolar quantities of $BeSO_4$ and $K_2SO_4$, together in water, and crystallizing by slow evaporation in a vacuum desiccator containing sulfuric acid. The double salt separated in the form of fine crystals. These were then dehydrated at 400°, a portion of the anhydrous material dissolved in water, and the beryllium determined by precipitation as hydroxide with ammonia, and ignition to BeO. The results were as follows.

| | |
|---|---|
| Weight of $BeSO_4 \cdot K_2SO_4$, g. | 2.5842 |
| Weight of BeO found, g. | 0.2319 |
| Ratio $BeSO_4/K_2SO_4$ calculated | 1.0021 |

A weighed portion of the anhydrous double sulfate, in a boat provided with a platinum cover (to avoid possible loss by spattering, because the double sulfate melts at 900°), was then placed in the reaction tube, and heated for six hours at 930°, the pressure of sulfur trioxide being set to 740 mm. The dissociation pressure of the double sulfate is given by Mlle. Marchal[4] as 806 mm., at 930°. The dissociation pressure of potassium sulfate at this temperature is undoubtedly very much less than 740 mm. After cooling and removing from the furnace, the boat was weighed, with the following result

| | |
|---|---|
| Weight of $BeSO_4 \cdot K_2SO_4$, g. | 2.2177 |
| Theoretical $SO_3$ loss, from $BeSO_4$ forming BeO, g. | 0.6346 |
| Actual $SO_3$ loss, g. | .6339 |

The contents of the boat were then treated with hot water, the insoluble BeO filtered off on a Gooch crucible and ignited to constant weight, with the following result

| | |
|---|---|
| Weight BeO found, g. | 0.1978 |
| Weight BeO calculated, g. | .1986 |

This experiment shows that the controlled decomposition of $BeSO_4 \cdot K_2SO_4$ results in the formation of BeO and $K_2SO_4$. At 930° the dissociation pressure of the basic $5BeO \cdot SO_3$ is apparently greater than 840 mm., as there was no indication of its formation.

**Series 14.** $PrO_2$–$La_2O_3$ Mixture.—It is evident from the behavior of all the mixtures of isomorphous sulfates, except those containing cerous sulfate, that the formation of solid solutions prevents the constituent sulfates from exerting their individual dissociation pressures and that the separation of the constituents is therefore impossible. The fact that cerous sulfate can be made to decompose preferentially in mixtures with others of the isomorphous rare earth sulfates is explainable as follows.

The dissociation pressure of a mixture of cerous, and, say, lanthanum sulfate, has some value intermediate between the dissociation pressures of pure $Ce_2(SO_4)_3$ and pure $La_2(SO_4)_3$, the precise value being dependent upon the composition of the mixture. If now the pressure of sulfur trioxide in the decomposition apparatus be set just above the dissociation pressure of pure $La_2(SO_4)_3$ at the temperature used, all the crystals will decompose into a mixture of $CeO_2$ and $La_2O_3$ because of the very great instability of $Ce_2O_3 \cdot SO_3$. Since $CeO_2$ and $La_2O_3$ (or any other rare earth sesquioxide) have crystal structures of quite different types,[20] the decomposition will thus have resulted in the breaking up of the solid solution, so that the mixture will consist of individual crystals of $CeO_2$ and $La_2O_3$. The $SO_3$ pressure in the apparatus being greater than the dissociation pressure of $La_2(SO_4)_3$, the $La_2O_3$ will recombine with $SO_3$ to form the normal sulfate, and a separation will have been effected.

The normal oxide in the rare earths is the sesquioxide. However, in addition to the known stable $CeO_2$, there is evidence of dioxide formation in the cases of praseodymium[21] and terbium.[20] In the case of praseodymium, it is impossible to obtain the sesquioxide by heating the nitrate, carbonate or oxalate, higher oxides approximating the composition $PrO_2$ being obtained. In order to get the sesquioxide, these higher oxides must be reduced by hydrogen at 600–800°.

It is evident that in order to obtain a separation by controlled sulfate decomposition, the solid solution of two isomorphous sulfates must be broken up. From Series 11, it is seen that such a break-up does not occur on heating a mixture of praseodymium and lanthanum sulfates, the

[20] Goldschmidt, Ulrich and Barth, *Skrifter utgitt av det Norske Videnskaps-Akademi i Oslo, I. Matem. Naturvid. Klasse*, No. 5, pp. 5–24 (1925), *Chemical Abstracts*, 19, 2764 (1925).

[21] Pagel and Brinton, THIS JOURNAL, 51, 42 (1929).

$Pr_2O_3 \cdot SO_3$ being a stable substance, in contradistinction to the cerous basic sulfate. Now since the heating of a mixture of the nitrates of praseodymium and lanthanum results in the formation of $PrO_2$ (at least in part) and $La_2O_3$, and since $PrO_2$ has a crystal structure similar to that of $CeO_2$, breaking up of the solid solution of $Pr(NO_3)_3$ and $La(NO_3)_3$ would be the result. The crystals of $PrO_2$ and $La_2O_3$ would still have to be separated, however, which would be very difficult. But if the mixed oxides were placed in the controlled decomposition apparatus, and the temperature set to some definite value, with sulfur trioxide provided from the decomposition of ferric sulfate, at a pressure less than that of pure $Pr_2(SO_4)_3$, but greater than that of $La_2(SO_4)_3$, the $PrO_2$ should form $Pr_2O_3 \cdot SO_3$, while the $La_2O_3$ should form $La_2(SO_4)_3$. Separation by solution of the latter would then be possible. The separation cannot be complete because some $Pr_2O_3$ will always be present. An experiment to test these considerations was therefore performed in the following manner.

About 0.3 g. each of anhydrous $Pr_2(SO_4)_3$ and $La_2(SO_4)_3$ were dissolved together in water, and oxalic acid added in slight excess, to precipitate the mixed oxalates. These were filtered off, and ignited to oxides. The oxides were dissolved in concentrated nitric acid, the solution evaporated down to small volume, transferred to a platinum crucible, and the evaporation continued to dryness. The crucible was then heated over a Méker burner until the evolution of the oxides of nitrogen ceased, after which it was placed in an electric muffle and heated at 400–450° for three hours. After cooling, the greater portion of the dark brown mixture of $PrO_2$–$Pr_2O_3$ and $La_2O_3$ was transferred to a boat and placed in the reaction tube. This boat was followed as in all the other runs, by another boat containing anhydrous ferric sulfate. The furnace, which had been previously set to maintain a temperature of 1010°, was then brought into position over the reaction tube, at such a rate that the evolution of sulfur trioxide from the ferric sulfate was just fast enough for the mixed oxides to absorb it, only a bubble or two per second escaping through the phosphoric acid by-pass into the absorption chambers, wherein the air pressure had been set to a pressure of 740 mm. At 1010° the dissociation pressures of $Pr_2(SO_4)_3$ and $La_2(SO_4)_3$ are 660 and 317 mm., respectively. When all the ferric sulfate had decomposed and no more sulfur trioxide escaped through the by-pass, the furnace was removed from over the reaction chamber, and the boat, the contents of which were now green in color, removed to a desiccator to cool, and then weighed. The boat was then again placed in the reaction tube, with a fresh charge of ferric sulfate, and the procedure described above repeated to make certain the complete conversion of the oxides to sulfates. A second weighing showed practically no change, so it was assumed that such was the case. It is interesting to note that the combination of the oxides with sulfur trioxide was quite rapid, it being necessary to subject them to its action for only about forty-five minutes for complete conversion to sulfates. This shows that the dissociation of the sulfates is readily reversible, and indicates the necessity for very rapid cooling after the removal of the furnace from the reaction tube, to "quench" the high-temperature equilibrium.

After the second weighing the boat was once more put into the decomposition chamber, and the mixed sulfates decomposed in the same manner as in all the other runs, the temperature and pressure being set at 1030° and 740 mm., respectively. Four hours' time was allowed for the completion of the decomposition, after which the boat was removed to a desiccator to cool, then weighed, with the results given.

| | |
|---|---|
| Composition of mixture, g. $Pr_2(SO_4)_3$ | 0.3019 |
| Composition of mixture, g. $La_2(SO_4)_3$ | .3105 |
| Weight of sulfates converted from oxides, g. | .5176 |
| $SO_3$ loss from these sulfates, after subtracting loss from $Ce_2(SO_4)_3$ impurity, g. | .0718 |
| Theoretical $SO_3$ loss, from $Pr_2(SO_4)_3$ forming $Pr_2O_3 \cdot SO_3$, g. | .0716 |

The contents of the boat were then treated with cold water. A portion dissolved, resulting in a practically colorless solution; the insoluble portion, which was quite green in color, was filtered off, treated with concentrated sulfuric acid, evaporated to dryness, and heated to constant weight at 600°. This resulted in 0.2558 g. of anhydrous $Pr_2(SO_4)_3$ and $La_2(SO_4)_3$. From this weight and the loss of sulfur trioxide, 0.235 g. of $Pr_2(SO_4)_3$ and 0.021 g. of $La_2(SO_4)_3$ were calculated to have decomposed.

That the greater part of the praseodymium had been concentrated into the insoluble portion was further indicated by a comparison of the absorption spectrum of this portion with that of the soluble portion. The former showed the bands of praseodymium quite distinctly, the latter only very faintly, when an approximately 5% solution of each, 10 cm. in thickness, was interposed between the Point-O-Lite and spectrograph. A further confirmation was obtained by comparing the arc spectrum of each portion with the spectrum of the original mixture.

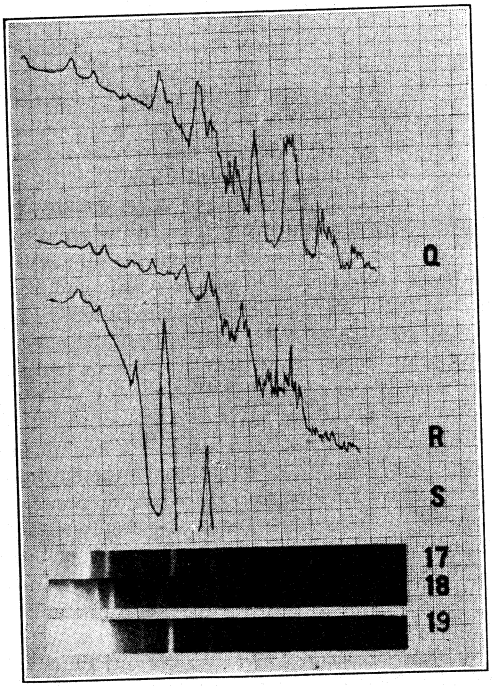


Fig. 8.—x-Ray diffraction by $La_2O_3$, $PrO_2$–$Pr_2O_3$, and a mixture of $La_2O_3$ and $PrO_2$–$Pr_2O_3$.

These results show that at least a partial separation of lanthanum and praseodymium can be made if a solid solution of their isomorphous salts be broken up into two solid phases, by the process of converting them to $La_2O_3$ and $PrO_2$ and then to $La_2(SO_4)_3$ and $Pr_2O_3 \cdot SO_3$.

**x-Ray Study of the $PrO_2$–$La_2O_3$ Mixture.**—A Hull–Debye–Scherrer powder tube (Reference 17a, page 487) was filled with some of the brown mixture of $PrO_2$, $Pr_2O_3$ and $La_2O_3$ obtained in the experiments of Series 14. This tube was then placed in a cassette on the x-ray apparatus, and exposed to the K radiation from a molybdenum target Coolidge tube for twenty-four hours, using a filament current

of 25 milliamperes. Another powder tube was half filled with some of the pure black $PrO_2$–$Pr_2O_3$ mixture obtained from Hilger, and half with pure $La_2O_3$ from the same source; an exposure of the same time and with the same filament current was then made.

The diffraction lines and their photometer curves are shown by Fig. 8, in which 17 and Q are from pure $PrO_2$–$Pr_2O_3$, 18 and R from pure $La_2O_3$ and 19 and S from the brown mixture of $PrO_2$ and $La_2O_3$. These x-ray photographs show very clearly that $PrO_2$ has a crystal structure decidedly different from that of $La_2O_3$, and that both $PrO_2$ and $La_2O_3$ crystals result from the thermal decomposition of the mixed nitrates and therefore confirm the conclusions drawn from the experiments of Series 14.

## Summary

1. The design and construction of a low-voltage electric high-temperature furnace using heating coils made of chromel wire and a photoelectrically operated thermostat capable of maintaining the furnace to within 0.1° of any desired temperature between 700 and 1100° have been described.

2. An all-glass-and-quartz apparatus for studying the decomposition of sulfates at high temperatures and at constant pressures of sulfur trioxide has been described.

3. The thermal decomposition of various binary mixtures of anhydrous sulfates formed by evaporation of mixed solutions has been studied. It has been found that mixtures of the non-isomorphous sulfates of ferric iron and zinc, aluminum and zinc, and beryllium and aluminum, may be preferentially decomposed so that the sulfate having the greatest dissociation pressure at a given temperature will be converted into an insoluble basic sulfate, or oxide, thus permitting a ready separation from the unchanged sulfate by solution of the latter in water.

4. Anhydrous mixed crystals of the isomorphous sulfates of nickel and cobalt, beryllium and zinc, beryllium and magnesium, lanthanum and praseodymium and neodymium and praseodymium were found to decompose into mixed crystals of basic sulfates or oxides, a separation being, therefore, impossible. The mixed crystals behave as a single phase, possessing a definite dissociation pressure at a given temperature, this pressure being intermediate between the dissociation pressures of the pure constituent sulfates and dependent on their relative amounts.

5. Cerous sulfate, in anhydrous mixtures with the isomorphous sulfates of lanthanum, praseodymium and neodymium, was found to be preferentially decomposable into $CeO_2$, as a consequence of the different crystal lattices of $CeO_2$ and the rare-earth sesquioxides.

6. The mixed nitrates of praseodymium and lanthanum decompose at 400–450° into the two solid phases $PrO_2$ and $La_2O_3$–$Pr_2O_3$; these oxides

may then be converted into $Pr_2O_3 \cdot SO_3$ and $La_2(SO_4)_3$–$Pr_2(SO_4)_3$ and a considerable separation effected by solution of the latter in water.

7. x-Ray diffraction photographs of some mixtures of oxides and of anhydrous sulfates, obtained by the Hull–Debye–Scherrer powder method, confirmed the conclusions drawn from the decomposition experiments, as to the formation of solid solutions.

ANN ARBOR, MICHIGAN

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

# CHEMICAL EFFECTS PRODUCED BY RADON ON THE SYSTEM: HYDROGEN–SULFUR–HYDROGEN SULFIDE[1,2]

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In connection with some recent work on the possible activation of hydrogen by alpha particle ionization[3] it was decided to investigate the synthesis of hydrogen sulfide by alpha particle ionization and to extend the work of Wourtzel[4] on the decomposition of hydrogen sulfide by radon. In a series of carefully conducted experiments Wourtzel found that the decomposition of hydrogen sulfide by alpha particle ionization was less efficient the higher the temperature. Since, in general, the efficiency of chemical reaction by alpha particle ionization is either independent of or increases with increasing temperature, it was thought that further investigation of this apparent exception would be of value. It seemed that the apparent decrease in the efficiency of the decomposition reaction at higher temperature might be due to a synthesis of hydrogen sulfide, both thermally and by ionization, which was itself more efficient as the temperature was increased.

It was therefore planned to conduct experiments on the synthesis and on the decomposition of hydrogen sulfide by alpha particle ionization to determine (1) the effect of increase of temperature, and therefore of sulfur vapor pressure, on the efficiency of the reactions, (2) the effect on this efficiency of varying the intensity of ionization and the amount of radon decomposed, and (3) if possible, something concerning the mechanism of the reactions which follow the initial act of ionization. It was felt that the

[1] Presented at the Buffalo Meeting of the American Chemical Society, September, 1931.

[2] This paper represents part of a thesis submitted by Edward C. Truesdale to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[3] E. C. Truesdale, *J. Phys. Chem.*, **34**, 2472 (1930).

[4] E. E. Wourtzel, *Le Radium*, **11**, 289–298, 332–347 (1919). See also S. C. Lind, "Chemical Effects of Alpha Particles and Electrons," 2d ed., The Chemical Catalog Co., New York, 1928.

experimental method best suited to the properties of the system being investigated was that of mixing the radon with the reactants in small sealed bulbs of known volume, and of determining the extent of the reaction by chemical analysis at the end of the experiment.

## Experimental Procedure

The Pyrex reaction bulbs were from 30 to 50 cc. in volume (about 4 cm. in diameter) and were provided at each end with a capillary tube about 10 cm. long. One of these capillaries was enlarged where it joined the bulb so that by making a clean break at this point the tiny bulb of radon and the sulfur could be introduced, after which the tube could be sealed on again without appreciably altering the volume of the bulb. Suitable constrictions at the ends of these tubes facilitated eventual sealing off and provided the readily breakable tips needed in the method of chemical analysis. The volume of each bulb was determined from time to time by filling it with mercury and weighing the latter; in spite of repeated use the volume of a bulb rarely changed by more than a few thousandths of a cubic centimeter. Since accurate knowledge of the volume of a bulb was especially important in the experiments on the decomposition of hydrogen sulfide, the volume was determined in each case at the end of the experiment.

After introducing the fragile bulb containing the radon and the 10 to 25 mg. pellet of sulfur into the reaction bulb and replacing the capillary tube, one end of the bulb was sealed onto the apparatus for filling it with the desired gas, the other end being similarly connected to a vacuum pump. The bulb was alternately filled with the gas and evacuated ten or twelve times, and (in the case of hydrogen) the gas was then allowed to flow through the bulb for several minutes before making final adjustment of pressure and sealing off the bulb. By careful shaking the tiny bulb of radon was then broken, thus allowing the radon to mix with the gas in the reaction bulb. In the experiments on the synthesis of hydrogen sulfide the bulb was then kept at room temperature for about five hours to allow the radon to come into equilibrium with its active deposit before starting the reaction, while in the experiments on the decomposition of hydrogen sulfide the reaction began as soon as the bulb of radon was broken, thus necessitating a correction for the fact that radioactive equilibrium had not been established.

The hydrogen used was purified in the manner described in a previous paper,[3] the same electrolytic source being used, while the sulfur was some of that previously purified by repeated distillation. The hydrogen sulfide was prepared in an all-glass apparatus by dropping fairly concentrated (1:1) phosphoric acid into 1 *M* sodium sulfide solution, and was purified by bubbling through a suspension of freshly precipitated ferrous sulfide, by passing over anhydrous calcium chloride and phosphorus pentoxide, and finally by double distillation from a trap cooled in liquid air into an evacuated 2-liter bulb. This storage bulb was connected to a mercury manometer, and by suitable stopcocks to the reaction bulb and vacuum line. The freshly-boiled mercury in the manometer did not react with this pure hydrogen sulfide over a period of several months, the surface of the mercury remaining perfectly bright as long as air was excluded. This fact is in accord with the work of Lilienfeld and White[5] and of Roberts[6] on the reaction of hydrogen sulfide with silver and with mercury, respectively. The sodium thiosulfate used in the titrations was recrystallized, the solution being standardized against resublimed iodine in the usual manner. The iodine solution was compared with the thiosulfate. The solutions were standardized frequently to correspond with the termination of an experiment. For the work on the synthesis of hydrogen sulfide

[5] Lilienfeld and White, THIS JOURNAL, **52**, 885 (1930).

[6] A. L. Roberts, *ibid.*, **53**, 1810 (1931).

these solutions were approximately 0.01 *N*, while for that on the decomposition they were 0.1 *N*.

The experiments at elevated temperatures were carried out by placing the bulbs in a small electrically-heated oven provided with thermostatic control, the temperatures being constant to ±1°. The temperatures chosen for the experiments on the synthesis of hydrogen sulfide were 37, 138, 185, 200, 234 and 270°. The first experiments were carried out at 200° in order to provide a sufficiently large vapor pressure of sulfur, without at the same time obtaining an appreciable thermal synthesis. The next series of experiments was conducted at 234°, because this temperature interval provided an approximately three-fold increase in the vapor pressure of sulfur, and because this was the lowest temperature at which the kinetics of the thermal synthesis of hydrogen sulfide had been measured in the classical experiments of Bodenstein,[7] and it was hoped that his results might be duplicated. It may be stated here that while the present experiments gave results of the same order of magnitude for the rate of thermal synthesis, lack of complete agreement is no doubt due to the fact that the different kinds of glass used affected the velocity of the surface reaction differently. The next experiments were conducted at 37° in order to establish the extent to which solid sulfur was entering into the ionized reaction. The marked decrease in the efficiency of the reaction thus obtained suggested that the vapor pressure of sulfur might be the most important variable factor in the reaction, and the experiments at the remaining temperatures were carried out to establish this point. The experiments on the decomposition of hydrogen sulfide were made last, at the four temperatures 37, 200, 234 and 270°. The vapor pressures of sulfur, taken from the recent work of Menzies and West,[8] are $1 \times 10^{-4}$, (*ca.*), 0.1, 1.1, 2.1, 7.6 and 23.0 mm. of mercury at the respective temperatures of 37, 138, 185, 200, 234 and 270°.

The following technique was observed in determining the amount of hydrogen sulfide in the bulbs. One stem of a bulb, fitted with a stopper, was placed in a 100-cc. flask provided with a side arm and containing the iodine solution, and the tip of the stem was then broken by pressing it against the bottom of the flask. By varying the air pressure in the flask the iodine solution was alternately forced into the bulb and removed several times, accompanied by shaking of the bulb, to insure complete absorption of the hydrogen sulfide. After breaking the other tip of the bulb the iodine solution was removed as completely as possible and the bulb was washed with a small portion of the thiosulfate solution and finally several times with distilled water. The excess iodine was then titrated with thiosulfate, the presence of colloidal sulfur in no way interfering with the determination of the end-point. While the titration of the hydrogen sulfide involved considerable transferring of the standard solutions, care was taken to make such a transfer quantitative, and blanks on the method were very satisfactory.

In general, each experiment on the synthesis of hydrogen sulfide was accompanied by one or more blank experiments in which no radon was used, in order to determine the correction to be applied for thermal synthesis. In the experiments on the decomposition of hydrogen sulfide several blank runs showed that no thermal decomposition of hydrogen sulfide occurred at 270°, the highest temperature employed, though there was a slight and constant decomposition produced by sealing off the reaction bulb from the filling system, for which correction was made.

## Calculation of Results

The details of the method of calculating the results of these experiments cannot be given here for lack of space, though such details are avail-

[7] M. Bodenstein, *Z. physik. Chem.*, **29**, 315 (1899).

[8] A. W. C. Menzies and W. A. West, *J. Phys. Chem.*, **33**, 1880 (1929).

able for anyone interested. The efficiency of the alpha particle in promoting chemical reaction is measured by determining the value of the ratio, $M/N$, of the $M$ molecules reacting to the $N$ ion pairs produced on the initial reactant molecules. $M$ was obtained from the results of the titration of hydrogen sulfide, while $N$ was calculated according to the method of Mund,[9] in conjunction with the general principles adopted by Lind.[4] The values of certain radioactive and physical constants are referred to here since they are different from those formerly used in such work.

**Definition of Terms.**—The radioactive constants adopted are those given by Meyer and Schweidler[10] as being the best values, and involve slight changes from the values formerly employed. The values of $\rho$ needed for the Mund factor $F$ were taken from a table prepared by Glockler, as yet unpublished, but differing only slightly from earlier values given by him.[11] Values of the specific ionization, $k$, and the stopping power, $s$, have not been determined experimentally for sulfur and for hydrogen sulfide, so that the best values obtainable on theoretical grounds were used. Discussion of these values would require too much space here, and while the values adopted differ slightly from those which would be obtained by using the method of Kleeman[12] for obtaining $k$, and of Glasson[13] for obtaining $s$, it is believed that they are very close to those which might be obtained experimentally. By combining the results of the present experiments on the synthesis of hydrogen sulfide at three different temperatures it was possible to show that the values adopted for sulfur on the assumption that the molecule was $S_8$ gave the most consistent results. Values of the specific ionization, $k$, were for hydrogen, 1.00, for sulfur, 1.1, for hydrogen sulfide, 1.18; values of the stopping power, $s$, were for hydrogen, 0.24, for sulfur, 7.0, and for hydrogen sulfide, 1.1. For a given composition of the reacting system, average values of $s$ were obtained by multiplying the value of this constant for each component by its partial pressure in the mixture, and adding the partial values thus obtained. In obtaining an average value of $k$ a similar procedure was employed, except that only the pressures of the initial reactants were considered.

In calculating the $M/N$ values it was necessary to employ an average pressure for each gas, and it was desired to obtain a weighted average pressure which, if maintained during an entire experiment, would yield the same total ionization as was actually produced in a gas whose composition was constantly changing. This was done by calculating an over-

[9] W. Mund, *Ann. Soc. Sci. Bruxelles*, **44**, 336 (1925); *J. Phys. Chem.*, **30**, 890 (1926).

[10] St. Meyer and E. Schweidler, *Radioaktivität*, 2d. ed., B/G Teubner, Berlin, 1927, pp. 411–439 and Table IV, Appendix.

[11] G. Glockler, *J. Phys. Chem.*, **31**, 1322 (1927).

[12] R. D. Kleeman, *Proc. Roy. Soc.* (*London*), **A79**, 220 (1907).

[13] J. L. Glasson, *Phil. Mag.*, [6] **43**, 477 (1922).

all value of the velocity constant, $k\mu/\lambda$,[14] and from this values of the pressure of each component were obtained for the times when one-fourth, one-half, and three-fourths of the total decomposition of radon had been completed. There was thus obtained an average composition of the gas mixture during each of these periods, and by averaging these with the initial and final compositions the desired weighted average was found. Such a calculation, carried out for a typical experiment on the decomposition of hydrogen sulfide, showed that the weighted average pressure of this gas was 99% of the arithmetical mean pressure. Such a weighted value was used in all experiments on the decomposition of hydrogen sulfide and in the experiments on its synthesis at 270°; in the remaining cases of synthesis where the extent of reaction was small, the arithmetical mean pressure was employed.

**Non-Equilibrium Decomposition of Radon.**—In calculating the number of ion pairs produced by radon it is usually assumed that the radon is in equilibrium with its decomposition products through radium C, and that therefore one obtains three times the number of alpha particles coming from radon alone. In the experiments on the decomposition of hydrogen sulfide and in certain of those on its synthesis it was impossible to attain this equilibrium before chemical reaction set in, and it was therefore necessary to find the number of alpha particles which were actually given off during the first four hours and eighteen minutes, the time $T$, after the radon bulb was broken. The result is as follows. Instead of obtaining decomposition of 0.03192 of the initial radon and of equal amounts of radium A and radium C during the time $T$, the amounts decomposed (expressed as a fraction of the initial number of radon atoms) were as follows

| | |
|---|---|
| No. $\alpha$-particles from Rn in time $T$ | $= 0.03192\ E_0 \cdot N_0$ |
| No. $\alpha$-particles from RaA in time $T$ | $= 0.03138\ E_0 \cdot N_0$ |
| No. $\alpha$-particles from RaC in time $T$ | $= 0.02324\ E_0 \cdot N_0$ |
| Total $\alpha$-particles in time $T$ | $= 0.08654\ E_0 \cdot N_0$ |

Dividing this total by 3 we obtain $0.028845\ E_0N_0$, a number which may be called the effective three-fold emission during the first four hours and eighteen minutes, and which is to be used in place of the equilibrium value $0.03192\ E_0 \cdot N_0$ in calculating the ionization during this time.

## The Synthesis of Hydrogen Sulfide

**Experimental Results.**—The results of the experiments on the synthesis of hydrogen sulfide are included in the following tables. In Tables I and II are to be found the experimental data and in Tables III and IV the derived values necessary to obtain the $M/N$ values given in the fifth column of Table IV. Since the thermal synthesis of hydrogen sulfide is primarily a surface reaction at all the temperatures employed except

[14] Lind, Ref. 4, p. 116.

at 270°, and since the amount of thermal reaction varies slightly from one bulb to another due to slight differences in surface activity, average values for the amount of thermal synthesis were used at each temperature below 270°, while at the latter temperature it was assumed that the reaction had become primarily a homogeneous one, in accordance with the work of Norrish and Rideal,[15] and the thermal correction to be made in each case was calculated on the basis of simple volume and pressure relationships. In Table II the amount of thermal synthesis is indicated in terms of a volume of 0.01 *N* iodine. The total synthesis, thermal plus ionization, may be found by adding the proper volume from Table II to the corresponding volume in the last column of Table III.

Due to some peculiarity of the oven which was used, the excess sulfur present in the reaction bulb collected as a small patch of liquid on the upper

TABLE I

EXPERIMENTAL DATA ON SYNTHESIS OF HYDROGEN SULFIDE

| Expt. | Reaction temp., °C. | Expt. time, hrs. | Bulb vol., cc. | Init. $P_{H_2}$, mm. | Init. temp., °C. | Init. Rn, mc. | *N*/100 $I_2$, corr., cc. |
|---|---|---|---|---|---|---|---|
| 1 | 200 | 186.27 | 48.85 | 685.5 | 25 | 57.7 | 7.16 |
| 2 | 200 | 206.59 | 34.45 | 696.5 | 25 | 54.9 | 6.68 |
| 3 | 200 | 204.42 | 41.52 | 699.5 | 25 | 56.0 | 6.87 |
| 4 | 200 | 203.92 | 48.75 | 702.5 | 23 | 130.2 | 13.11 |
| 5 | 200 | 209.51 | 51.87 | 693.0 | 27 | 105.7 | 11.10 |
| 6 | 234 | 160.25 | 33.19 | 729.1 | 22 | 62.0 | 8.42 |
| 7 | 234 | 156.25 | 30.60 | 731.6 | 22 | 63.6 | 7.88 |
| 8 | 234 | 156.25 | 31.36 | 729.1 | 22 | 57.3 | 7.18 |
| 9 | 37 | 211.00 | 41.52 | 729.0 | 23 | 56.2[a] | 0.13 |
| 10 | 37 | 211.75 | 48.75 | 727.5 | 23 | 43.6[a] | .26 |
| 11 | 270 | 120.00 | 34.36 | 712.2 | 26 | 73.9 | 16.90 |
| 12 | 270 | 130.50 | 33.19 | 717.2 | 26 | 70.6 | 16.66 |
| 13 | 138 | 144.00 | 48.78 | 710.2 | 25 | 66.5[a] | 1.02 |
| 14 | 138 | 122.00 | 48.62 | 710.2 | 25 | 72.2[a] | 1.03 |
| 15 | 185 | 93.00 | 34.36 | 707.3 | 25 | 89.4[a,b] | 6.84 |
| 16 | 185 | 141.50 | 34.30 | 706.4 | 25 | 71.4[a,b] | 6.76 |

[a] Correction made for attainment of radioactive equilibrium during first four hours eighteen minutes. [b] Reaction bulbs cooled to room temperature for three hours while repairing thermostat during the experiment. Radon decomposed during this three hours not counted.

TABLE II

CORRECTIONS FOR THERMAL SYNTHESIS OF $H_2S$

| Expt. | Temp., °C. | *N*/100 iodine, cc. | Expt. | Temp., °C. | *N*/100 iodine, cc. |
|---|---|---|---|---|---|
| 1, 2, 3, 4, 5 | 200 | 0.39 | 12 | 270 | 19.18 |
| 6, 7, 8 | 234 | 1.68 | 13, 14 | 138 | 0.12 |
| 9, 10 | 37 | 0.00 | 15 | 185 | .16 |
| 11 | 270 | 19.87 | 16 | 185 | .29 |

[15] R. Norrish and E. Rideal, *J. Chem. Soc.*, **123**, 696, 1689, 3203 (1923).

TABLE III

CALCULATED DATA FOR SYNTHESIS OF HYDROGEN SULFIDE

| Expt. | Total vol. $H_2S$, cc. | Av. $P_{H_2}$, mm. | Av. $P_{H_2S}$, mm. | $P$ sulfur, mm. | $H_2S$ formed, % |
|---|---|---|---|---|---|
| 1 | 0.85 | 678.3 | 7.2 | 2.1 | 2.10 |
| 2 | .79 | 687.0 | 8.9 | 2.1 | 2.74 |
| 3 | .81 | 691.4 | 8.1 | 2.1 | 2.32 |
| 4 | 1.51 | 689.7 | 12.8 | 2.1 | 3.64 |
| 5 | 1.29 | 682.6 | 10.4 | 2.1 | 2.99 |
| 6 | 1.13 | 708.0 | 21.1 | 7.6 | 3.84 |
| 7 | 1.07 | 710.0 | 21.6 | 7.6 | 3.93 |
| 8 | 0.99 | 709.0 | 20.1 | 7.6 | 3.56 |
| 9 | .01 | 729.0 | 0.0 | $1 \times 10^{-4}$ | 0.04 |
| 10 | .03 | 727.5 | .0 | $1 \times 10^{-4}$ | .07 |
| 11 | 4.12 | 655.7 | 56.5 | 23.0 | 14.0 |
| 12 | 4.01 | 660.2 | 57.0 | 23.0 | 14.0 |
| 13 | 0.13 | 709.1 | 1.1 | 0.1 | 0.31 |
| 14 | .13 | 709.1 | 1.1 | .1 | .31 |
| 15 | .78 | 697.8 | 9.5 | 1.1 | 2.68 |
| 16 | .79 | 696.8 | 9.6 | 1.1 | 2.70 |

TABLE IV

CALCULATED RESULTS OF SYNTHESIS OF HYDROGEN SULFIDE

| Expt. | $+M_{H_2S} \times 10^{-19}$ | $N_{H_2+S} \times 10^{-19}$ | Rn decomp., mc. | $\frac{+M_{H_2S}}{N_{H_2+S}}$ | Reaction temp., °C. |
|---|---|---|---|---|---|
| 1 | 2.17 | 1.97 | 43.5 | 1.10 | 200 |
| 2 | 2.02 | 1.79 | 43.3 | 1.13 | 200 |
| 3 | 2.08 | 1.93 | 44.0 | 1.08 | 200 |
| 4 | 3.97 | 4.80 | 102.3 | 0.83 | 200 |
| 5 | 3.36 | 3.95 | 84.0 | .85 | 200 |
| 6 | 2.55 | 2.26 | 43.5 | 1.13 | 234 |
| 7 | 2.39 | 2.14 | 44.1 | 1.12 | 234 |
| 8 | 2.18 | 1.91 | 37.4 | 1.14 | 234 |
| 9 | 0.04 | 1.83 | 44.6 | 0.02 | 37 |
| 10 | .08 | 1.50 | 34.7 | .05 | 37 |
| 11 | 5.12 | 3.44 | 44.1 | 1.49 | 270 |
| 12 | 5.05 | 3.42 | 44.2 | 1.48 | 270 |
| 13 | 0.31 | 1.86 | 43.9 | 0.17 | 138 |
| 14 | .31 | 1.78 | 43.3 | .17 | 138 |
| 15 | 2.07 | 1.87 | 46.3 | 1.11 | 185 |
| 16 | 2.05 | 1.88 | 46.7 | 1.09 | 185 |

surface of the bulb, and since approximately the same excess of sulfur was present in all of the experiments, the area of this patch was always very nearly the same. Consideration of the possibility of loss of ionization through trapping or dissolving of radon and its active deposit in this liquid sulfur showed that under the conditions of the experiments such loss would be entirely negligible.

**Discussion of Results.**—In all but two cases the same amount of radon was decomposed in each experiment, in order to obtain suitable data for

determining the temperature coefficient of the $M/N$ values. Neglecting Experiments 4 and 5, the average $M/N$ at each temperature was plotted against the temperature as shown in the lower curve of Fig. 1. The peculiar irregularity of this curve suggests that it is not the temperature which should be plotted against $M/N$ values, but rather the vapor pressure of sulfur, and by plotting the vapor pressure of sulfur at each temperature against the $M/N$ values the upper curve in Fig. 1 is obtained. The shape of this curve is readily explained by a consideration of the processes involved in the reaction. At a negligible pressure of sulfur nearly all the ionization produced by the alpha particles must fall on the hydrogen, and

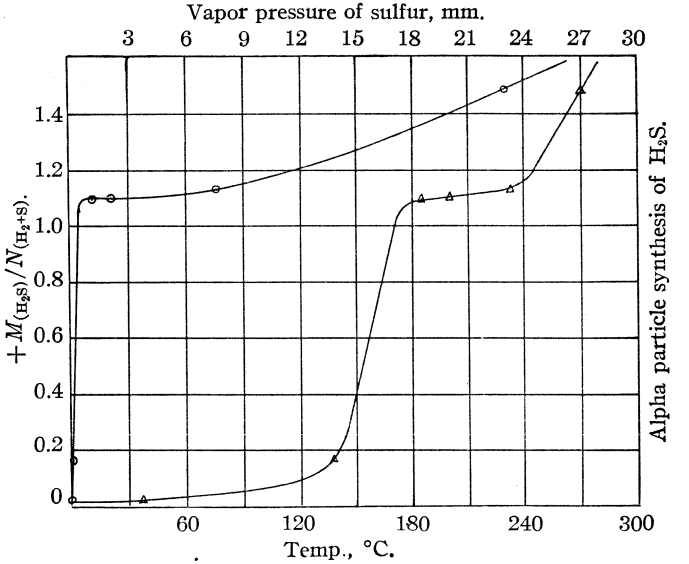


Fig. 1.—⊙, $M/N$ as a function of vapor pressure of sulfur; △, $M/N$ as a function of temperature.

in the absence of an appreciable number of sulfur molecules the chief event that can occur is the recombination of hydrogen ions and electrons, with little resultant chemical reaction. As the vapor pressure of sulfur increases with higher temperature, more sulfur molecules will be available to partake in whatever series of reactions is responsible for the formation of hydrogen sulfide. Over quite a range of pressure we should expect a marked increase in the efficiency of the chemical reaction up to the point where there is a sufficient concentration of sulfur molecules to utilize the ionization energy with maximum efficiency. Also there should at all times be a gradual increase in yield with increase in sulfur vapor pressure since more and more ionization will fall directly on the sulfur in addition to the constant amount falling on the hydrogen. Moreover, as the tem-

perature rises above, say, 234°, the efficiency of the chemical part of the reaction should increase just as it does in the thermal synthesis of hydrogen sulfide, and one would expect a marked increase in $M/N$ values on this account. That this is exactly the case may be seen from the upper curve of Fig. 1. Under the experimental conditions it appears that a vapor pressure of 1 mm. of sulfur is sufficient to utilize the ionization falling on the hydrogen with maximum efficiency.

In the experiments at 200° three very different amounts of radon were decomposed, and the result of this variation may best be seen by plotting the $M/N$ values against the amount of radon decomposed or, since the duration of all these experiments was the same, against the percentage of the total possible hydrogen sulfide which had been formed. The latter method gave irregular results, so that the curves in Fig. 2 were drawn through points obtained by the former method, the three values corresponding to the smallest amount of decomposition having been averaged. Extrapolation to an initial $M/N$ value is inaccurate, but this value cannot be less than 1.3 nor more than 2.0. The points lie on the straight line to within the limit of accuracy of the experiments; however, if the curve is to be similar to that obtained later in the *decomposition* of hydrogen sulfide, the broken curve would be preferred. One would immediately suspect that the decrease in $M/N$ values with increase in the extent of reaction is due to the back reaction produced by ionization falling on the ever-increasing amount of hydrogen sulfide. However, if one calculates the extent of this back reaction, using an average pressure of hydrogen sulfide, it is found to be insufficient to account for all of the observed decrease in the $M/N$ values. The upper curves of each kind in Fig. 2 are for $M/N$ values which have been corrected for back reaction due to the ionization of hydrogen sulfide.

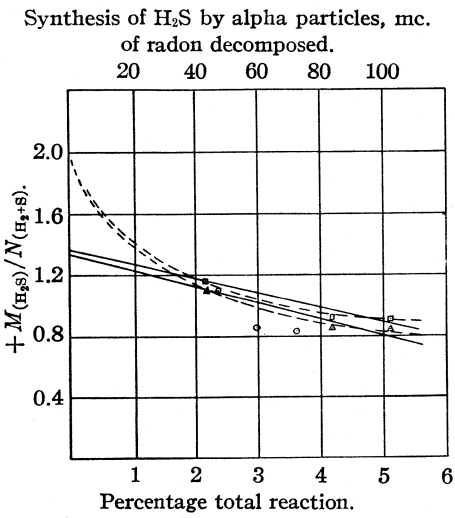


Fig. 2.—△, $M/N$ as a function of radon decomposed; ⊡, same as △ but with $M/N$ corrected for back reaction; ⊙, $M/N$ as a function of extent of reaction, no curve through these points.

A second possible explanation of the decrease in $M/N$ values with increased extent of reaction would be that the efficiency of the synthesis of hydrogen sulfide is dependent on the intensity of ionization. The chief basis for such an assumption lies in the fact that the vapor pressure of

sulfur is so low at 200°. Thus, by whatever mechanism the reaction proceeds, the presence of a small concentration of sulfur vapor would result in a certain efficiency of synthesis at one intensity of ionization, but this concentration of sulfur might be insufficient to play an equally efficient role if the intensity of ionization were greatly increased, since relatively more hydrogen ions would then recombine with electrons. Consideration of the nature of radioactive transformation shows that since the duration of each experiment was very nearly the same, the intensity of ionization would be proportional to the amount of radon *decomposed* (and also to the initial amount of radon). The relation between $M/N$ and ionization intensity might be expressed in the following form

$$M/N = (M/N)_0 - kE$$

where $(M/N)_0$ is the initial $M/N$ value for the pure reactants and may be assumed to be independent of ionization intensity, and $E$ is the amount of radon decomposed. By combining Experiments 3 and 4, $k$ is found to be equal to 0.0043, and $(M/N)_0$ becomes 1.27, slightly less than the value obtained earlier by straight line extrapolation in Fig. 2. Assuming the values of these constants, calculated values of $M/N$ were obtained for Experiments 1, 2 and 5 which differed from the experimental values by less than 4%. On the basis of the above equation the dependence of $M/N$ upon ionization intensity might be attributed to an abnormal back reaction, whereby the decomposition of hydrogen sulfide would be proportional not only to its own concentration (the normal case) but also to the intensity of ionization. The latter relation might be explained on the basis of exchange ionization, with the ionization flowing onto the hydrogen sulfide molecules from the hydrogen ions. An increase in the intensity of ionization would favor the latter process at the expense of reaction with negative sulfur ions. Other equations may be made to fit the data, however, and other explanations advanced, so that for the present we must be content to state that back reaction, calculated in the normal way, is not sufficient to account for the observed decrease of $M/N$ values with increased extent of reaction.

It was desirable to know how much of the synthesis of hydrogen sulfide was due to processes occurring in the gas phase and how much was due to reaction on the surface of the excess sulfur. Accordingly, in the two experiments at 37°, sulfur was carefully distilled *in vacuo* onto the surface of each bulb, so that in one case 6 sq. cm. (the area normally covered in the other experiments) and in the other case 74.5 sq. cm. of surface were covered. The ratio of surfaces covered is thus roughly 1:12, in Experiments 9 and 10. By reference to Table IV it is seen that the $M/N$ values were 0.021 and 0.053, respectively, showing that the extent of sulfur surface does affect the reaction. It is difficult to account for this effect on the assumption that sulfur was removed from the gas phase in the ionized

reaction faster than it could be supplied by evaporation from the wall, since the experiments lasted 211 hours and the total amount of reaction was so small. The alternative is to assume that the reaction occurred partly in the gas phase and partly on the wall, the first rate being constant in the two cases, and that of the second being in proportion to the area of sulfur exposed. Thus, if the gas phase reaction gave an $M/N$ of 0.018 in each case, the $M/N$ for the surface reaction would be 0.003 in one case and $12 \times 0.003$ or 0.036 in the other case, thus giving the observed $M/N$ values of 0.021 and 0.053. We may thus conclude that the amount of surface reaction occurring in all experiments on the synthesis of hydrogen sulfide at elevated temperatures was negligible in comparison with that occurring in the gas phase.

**Mechanism of the Synthesis of Hydrogen Sulfide.**—In attempting to picture a mechanism for the synthesis of hydrogen sulfide in the presence of radon, one may assume such reaction to be entirely ionic, or to be in the nature of a chemical reaction following the formation or recombination of the ions. In the latter case it would be logical to assume that, at least in part, the same mechanism was effective as is known to govern the purely thermal reaction. From the work of Norrish and Rideal[15] it appears that the thermal reaction $H_2 + S = H_2S$ begins as a surface reaction and that the homogeneous reaction rate only becomes equal to the former at about 285°. Hence in the present experiments, except at 270°, the thermal synthesis which is occurring will not be directly related to the synthesis by ionization which is occurring only in the vapor phase. The consensus of opinion of those who have studied the thermal synthesis of hydrogen sulfide seems to be that the homogeneous reaction mechanism is probably as follows

$$S_8 = 4S_2 \text{ (probably stepwise)}$$
$$S_2 \doteq 2S \ (-103{,}000 \text{ cal.})$$
$$H_2 + S = H_2S$$

It is assumed that the slow reaction whose velocity is measured is the dissociation of $S_2$, thus accounting for the agreement between the apparent activation energy of the third step and the dissociation energy of $S_2$ (103,000/2 or 51,000 cal.). Thus the final equation for the reaction is

$$\frac{+d(H_2S)}{dt} = k(H_2)\,(S) = k_1k_2(H_2)\,\sqrt[8]{S_8}$$

One might then assume that the function of ionization in promoting this reaction is to increase the concentration of sulfur atoms and also, by increasing the energy of the reactants, to increase the rate at which they react. But it is not sufficient to limit the reaction to this one mechanism. It is certain that atomic hydrogen is produced under such intense ionization, and it has been shown by Bonhoeffer[16] that sulfur can react with atomic

[16] K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

hydrogen at room temperature to produce hydrogen sulfide. Thus an equation expressing the rate of synthesis by ionization would in its simplest form be of the type

$$\frac{+d(H_2S)}{dt} = k_1(H_2)\,(S) + k_2(H)\,(S_x)$$

neglecting any purely thermal reaction.

In an attempt to set up a kinetic equation which would express the rate of formation of hydrogen sulfide as a function of the concentration of the more important constituents of the system, including that of radon and of hydrogen and sulfur atoms, a list was made of all the reactions which might occur, and from this group of more than thirty possible reactions the ten or twelve most probable ones were selected. Thus far it has not been possible to secure such an equation in useful form; moreover, the present data are not well suited for insertion into such an equation except in its integrated form, and further data will be needed. We may, however, consider the various mechanisms (the ionic and the atomic, chiefly) proposed as they would be related to changes in the experimental conditions. This may best be done by considering the effect produced on the efficiency of the reaction ($M/N$ value) by altering the conditions of the experiment. The chief reactions to be considered are the following

$$H_2 + \alpha \longrightarrow H_2^+ + (-) \quad (1)$$
$$S_8 + \alpha \longrightarrow S_8^+ + (-) \quad (2)$$
$$H_2^+ + (-) \longrightarrow H_2 + h\nu;\ \text{or H + H with some excess energy available} \quad (3)$$
$$S_8^+ + (-) \longrightarrow S_{(8-n)} + nS \quad (4)$$
$$S_8 + (-) \longrightarrow S_8^- \quad (5)$$
$$H_2^+ + S_8^- \longrightarrow H_2S + S_7\ (\text{or } S_6 + S) \quad (6)$$
$$H_2 + S \longrightarrow H_2S \quad (7)$$
$$H + S_8 \longrightarrow H_2S + S_7\ (\text{or } S_6 + S) \quad (8)$$

Reaction 6 represents the synthesis of hydrogen sulfide by a purely ionic mechanism, in which clustering might or might not occur, while reactions (7) and (8) represent synthesis due to chemical reactions which depend on ionization for their supply of atomic reactants.

**Effect of Increase of Temperature.**—The primary effect of increasing the temperature is to increase the vapor pressure of sulfur, hence in general it is the latter which must be considered. Increase in temperature should have little effect on the efficiency of the reaction if it proceeds by a strictly ionic mechanism, and below 234° it should have no marked effect on any of the steps involved in a *chemical* reaction which follows neutralization of the ions. The fact that a pronounced increase in $M/N$ values does appear above 234° would indicate that a simple ionic or clustering mechanism either is not involved at lower temperatures, or that above this temperature it is augmented by secondary chemical reactions which are temperature sensitive.

**Effect of Increase of Sulfur Vapor Pressure.**—Increase in the vapor pressure of sulfur will, of course, cause an increase in the ionization falling on the sulfur, this increase being duly taken into account in calculating $N$. In addition, an increase in the concentration of sulfur would make more efficient the trapping of electrons by sulfur, thus preventing their direct recombination with hydrogen ions. This fact would certainly increase the efficiency of formation of hydrogen sulfide according to a clustering or ionic mechanism. According to an atomic (chemical) mechanism the only adverse effect of increasing the concentration of sulfur would be a decrease in the number of hydrogen atoms formed; however, the number of sulfur atoms formed would increase approximately as the square of the sulfur concentration, and since the reaction between hydrogen molecules and sulfur atoms is one of the chief chemical steps to be considered there would still be a marked increase in the efficiency of the reaction with increase in concentration of sulfur. The assumption is, of course, made that the vapor pressure of sulfur is so small that any of the reactions considered would be sensitive to small actual, but large relative changes of this pressure.

**Effect of Intensity of Ionization.**—The relation of the efficiency of hydrogen sulfide formation to the intensity of ionization has already been discussed, and the decrease in the value of $M/N$ with increase in ionization intensity was attributed to an unfavorable shift in the competition between hydrogen ions and sulfur molecules for the electrons, assuming an ionic mechanism. Such a shift in the competition would tend to increase the number of hydrogen atoms being formed, but with only a small constant number of sulfur molecules available, a larger fraction of these hydrogen atoms would have to recombine without producing chemical reaction. Further consideration shows that any of the more probable mechanisms must suffer a decrease in efficiency as long as the concentration of sulfur remains critically small. The lack of suitable information concerning collision diameters, electron speeds, efficiency of ion recombination, etc., precludes any attempt to verify the above suggestions by calculating concentration changes which would be produced if the intensity of ionization were altered.

In conclusion, it may be said that while there is no basis for insisting upon any one mechanism for the synthesis of hydrogen sulfide in the presence of radon, a consideration of the complex situation existing in such a system indicates that both an ionic (clustering) mechanism and a chemical (atomic) mechanism may and probably do occur simultaneously. Since the $M/N$ value showed a marked increase at 270° over that at 234°, one might conclude that as the temperature is increased that reaction which is similar to the homogeneous thermal reaction becomes more important. Certainly one cannot assume that the size of the ion cluster increases with temperature; however, it is also possible that the added

thermal energy enables more of the cluster to react chemically at the instant of neutralization.

## The Decomposition of Hydrogen Sulfide

Two experiments were conducted at 37°, decomposing in each case about 75 millicuries of radon, in order to obtain data to supplement the results reported by Wourtzel. Two experiments each were carried out at 200, 234 and 270° and at each temperature the attempt was made to decompose about 20 mc. of radon in one case and about 75 mc. in the other, thus providing data for a study of the temperature coefficient and of the relation of $M/N$ to the extent of reaction.

The calculations were carried out in the same manner as were those on the synthesis of hydrogen sulfide. The experimental data needed for the calculation of the $M/N$ values are given in Table V. It should be recalled that in all these experiments correction had to be made for the non-equilibrium decomposition of radon during the first four hours and eighteen minutes. The $M/N$ values obtained in these experiments are given in Table VI. Interpretation of these results must be postponed until we have considered the results obtained by Wourtzel.

TABLE V

EXPERIMENTAL DATA ON DECOMPOSITION OF HYDROGEN SULFIDE

| Expt. | Bulb vol., cc. | Init. $P_{H_2S}$, mm. | Init. temp., °C. | Init. radon, mc. | React. temp., °C. | Expt. time, hrs. | $N/10$ iodine, cc. |
|---|---|---|---|---|---|---|---|
| 1 | 41.49 | 705.8 | 28.5 | 83.2 | 37 | 257.50 | 21.08 |
| 2 | 51.82 | 705.8 | 28.5 | 85.9 | 37 | 258.00 | 27.78 |
| 3 | 34.38 | 737.9 | 32.0 | 92.0 | 200 | 231.25 | 17.65 |
| 4 | 31.40 | 733.9 | 32.0 | 54.8 | 200 | 69.75 | 20.49 |
| 5 | 48.71 | 729.7 | 29.0 | 50.0 | 234 | 69.30 | 33.80 |
| 6 | 48.82 | 729.7 | 29.0 | 75.0 | 234 | 240.31 | 29.38 |
| 7 | 48.73 | 727.3 | 24.0 | 95.3 | 270 | 192.67 | 29.08 |
| 8 | 52.16 | 729.3 | 24.0 | 40.0 | 270 | 103.50 | 36.70 |

TABLE VI

CALCULATED RESULTS ON DECOMPOSITION OF HYDROGEN SULFIDE

| Expt. | $H_2S$ decomp., cc. | Av. $P_{H_2S}$, mm. | Av. $P_{H_2}$, mm. | $H_2S$ decomp., % | Mc. Rn decomp. | $M_{H_2S} \times 10^{-19}$ | $N_{H_2S} \times 10^{-19}$ | $-M_{H_2S}/N_{H_2S}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 11.17 | 585.9 | 120.9 | 32.0 | 71.1 | 30.20 | 11.46 | 2.63 |
| 2 | 12.35 | 598.9 | 106.9 | 28.4 | 73.6 | 33.41 | 13.50 | 2.48 |
| 3 | 10.00 | 607.0 | 130.9 | 33.5 | 75.6 | 27.06 | 12.05 | 2.25 |
| 4 | 4.09 | 670.2 | 63.7 | 15.1 | 22.3 | 11.09 | 4.10 | 2.70 |
| 5 | 4.40 | 684.8 | 44.9 | 10.4 | 20.2 | 11.91 | 4.88 | 2.44 |
| 6 | 9.46 | 641.7 | 88.0 | 22.4 | 62.6 | 25.59 | 13.39 | 1.91 |
| 7 | 10.29 | 633.6 | 93.7 | 24.0 | 72.7 | 27.76 | 17.44 | 1.59 |
| 8 | 4.89 | 683.6 | 45.7 | 10.6 | 21.6 | 13.23 | 6.09 | 2.17 |

**Experiments of Wourtzel.**—Wourtzel[4] studied the decomposition of hydrogen sulfide when mixed with radon in small bulbs of about 40 cc.

capacity (4.3 cm. diameter). Using a rather elaborate apparatus, he followed the course of the reaction by freezing out the hydrogen sulfide and radon from time to time and measuring the pressure of the residual hydrogen, estimating his error in such measurements at about 1%. At the end of each interval the residual hydrogen was pumped off, so that each experiment was begun with pure hydrogen sulfide and, since the extent of reaction was small, the gas was at all times practically pure. In this respect his experiments differed from the present ones, where significant pressures of hydrogen were produced. Wourtzel used smaller initial quantities of radon and the duration of each experiment was much shorter than in the present work. One would thus expect Wourtzel's $M/N$ values to be higher than those obtained in the present experiments, and the former may be regarded as approximately the upper limit for the $M/N$ ratio. Wourtzel expressed all his results in terms of the number of molecules of hydrogen sulfide decomposed per ion pair when the gas was at "infinite pressure," *i. e.*, at a pressure sufficiently great to utilize the complete path of an (average) alpha particle. His actual pressures varied from 1.5 to 12 atmospheres, being about 2 atmospheres in most of his experiments. Since a number of the radioactive constants and ionization factors have been revised since his experiments were performed, his results have been recalculated by the same method as that employed in obtaining $M/N$ values in the present experiments. The first five columns of Table VII are taken directly from Wourtzel's data, and the values in the last three columns are those obtained in the process of recalculation. The gas was assumed to be pure hydrogen sulfide at all times, the corresponding values of $k$ and $s$ being used. The factor necessary to account for the recoil atom effect was found to be 1.02 at a pressure of 1 atmosphere in bulbs of the size employed by Wourtzel. At 1.5 atmospheres this factor was 1.015; at 2 atmospheres, 1.01; at 4 atmospheres, 1.005; at higher pressures the recoil atom effect was neglected. In Table VII $T$ is the time in hours, $p$ is the average pressure of an experiment in atmospheres, $v$ is cc. of hydrogen sulfide decomposed (N. T. P.). The sets of Experiments I and II were run simultaneously, a single charge of radon being divided between the two bulbs; one bulb was kept at room temperature while the temperature of the other was occasionally elevated in order to obtain a temperature coefficient for the reaction.

It should be noted that Wourtzel calculated his results in terms of a reaction constant, $KQ_0/\lambda$, and then determined his value of $M/N$ from the average value of this constant in each series. It thus appeared that the decomposition of hydrogen sulfide by alpha particle ionization was less efficient at the higher temperatures. However, when each separate experiment is used to obtain a value of $M/N$, as in the present recalculation, it is found that the very values needed to establish this temperature coefficient

TABLE VII

RECALCULATION OF WOURTZEL'S RESULTS

| No. | $t$, °C. | $T$ | $p$ | $v$ | $H_2S$ decomp., % | Mc. Rn. decomp. | $-M_{H_2S}/N_{H_2S}$ |
|---|---|---|---|---|---|---|---|
| Expt. I: vol. bulb, 43.49 cc.; initial radon, 58.23 mc. | | | | | | | |
| 1 | 18 | 15.00 | 2.055 | 4.200 | 4.69 | 6.23 | 3.59 |
| 2 | 18 | 24.15 | 1.940 | 5.315 | 6.30 | 8.67 | 3.40 |
| 3 | 18 | 24.45 | 1.828 | 4.213 | 5.30 | 7.30 | 3.36 |
| 4 | 18 | 16.55 | 1.733 | 3.286 | 4.35 | 4.03 | (4.83) |
| 5 | 18 | 104.15 | 1.593 | 8.296 | 11.92 | 17.31 | 3.02 |
| 6 | 18 | 39.00 | 1.474 | 1.650 | 2.57 | 3.69 | 3.01 |
| 7 | 18 | 79.35 | 1.430 | 2.013 | 3.23 | 4.86 | (2.89) |
| Expt. II: vol. bulb, 41.00 cc.; initial radon, 54.77 mc. | | | | | | | |
| 1 | 18 | 15.45 | 2.172 | 4.000 | 4.50 | 6.03 | 3.36 |
| 2 | 18 | 24.45 | 2.054 | 5.195 | 6.20 | 8.21 | 3.36 |
| 3 | 18 | 24.55 | 1.923 | 4.176 | 5.30 | 6.85 | 3.38 |
| 4 | 220 | 16.45 | 1.819 | 2.273 | 3.0 | 3.93 | (3.36) |
| 5 | 18 | 104.15 | 1.706 | 8.200 | 11.72 | 16.19 | 3.09 |
| 6 | 220 | 59.15 | 1.590 | 1.218 | 1.86 | 4.88 | (1.60) |
| 7 | 95 | 79.85 | 1.556 | 1.730 | 2.70 | 3.92 | (2.91) |
| Expt. III: vol. bulb, 41.00 cc.; initial radon, 56.4 mc. | | | | | | | |
| 1 | 18 | 24.35 | 1.928 | 5.300 | 6.72 | 9.47 | 3.11 |
| 2 | 18 | 25.60 | 1.816 | 4.362 | 5.86 | 8.25 | 3.08 |
| 3 | 18 | 22.80 | 4.009 | 4.634 | 2.82 | 6.12 | 3.11 |
| 4 | 18 | 25.60 | 3.900 | 4.358 | 2.73 | 5.72 | 3.15 |
| 5 | 18 | 22.90 | 6.468 | 3.676 | 1.38 | 4.28 | 3.23 |
| 6 | 18 | 24.00 | 6.356 | 3.460 | 1.33 | 3.74 | 3.49 |
| 7 | 18 | 18.30 | 9.107 | 2.774 | 0.74 | 2.94 | 3.41 |
| 8 | 18 | 22.50 | 11.92 | 1.552 | .32 | 2.04 | 2.69 |
| 9 | 18 | 54.80 | 11.88 | 3.307 | .68 | 4.67 | 2.50 |

are not in good agreement with others at the same temperature. These values are the ones marked in parentheses in Table VII. One or two general conclusions may be drawn from his results before proceeding to a comparison with the results obtained in the present experiments. In the set of Experiments I, Table VII, there seems to be a trend toward lower $M/N$ values as the reaction proceeds. The set of Experiments III is intended to show the effect of change of pressure on the $M/N$ values; there seems to be a slight increase in $M/N$ as the pressure increases (excepting the last two values), but equally high $M/N$ values were obtained in Experiments I and II at only 2 atmospheres pressure, so that within the limits of error of the experiments it may be said that increase of pressure (at high pressure) has no effect on the efficiency of the reaction.

One additional point remains to be considered before proceeding to detailed analysis of the results. The temperatures employed by Wourtzel were 18, 95 and 220°, while in the present experiments the temperatures

were 37, 200, 234 and 270°. The lower temperatures may be considered equivalent, since there are no thermal effects involved in the system at room temperature. The remaining temperatures in the present work were, of course, chosen to correspond to those used in the synthesis of hydrogen sulfide. However, since Wourtzel's $M/N$ values at the higher temperatures seem to be less trustworthy, and since the present results are in logical agreement with one another, the choice of different temperatures is not a serious matter.

## Discussion of Combined Results

**Effect of Extent of Decomposition on $M/N$ Values.**—Comparable $M/N$ values may be obtained only from systems having approximately the same composition, and one must then express $M/N$ values as a function of the amount of radon decomposed (since all experiments began with pure hydrogen sulfide), or if it is necessary to consider the thermal reaction also, as a function of the composition of the system. In Table VIII Wourtzel's most consistent $M/N$ values at 18°, together with the two values obtained in the present experiments at 37°, are arranged in the order of increasing amount of radon decomposed and also of increasing per cent. decomposition of hydrogen sulfide. These values were averaged as indicated in the table, and the average values when plotted gave the smooth curve numbered I in Figs. 3 and 4. It is at once evident that the initial $M/N$ value should be between 3.75 and 4.0, and that as the composition of the gas changes the *synthesis* of hydrogen sulfide becomes more and more important, resulting in a progressive lowering of the effective $M/N$ for decomposition.

TABLE VIII

$M_{H_2S}/N_{H_2S}$ AS FUNCTION OF EXTENT OF REACTION

Wourtzel, experiments at 18°

| Expt. | Press., atm. | Radon decomp. | Av. Rn decomp. | $H_2S$ decomp., % | Av. % decomp. | $M_{H_2S}/N_{H_2S}$ | Av. $M_{H_2S}/N_{H_2S}$ |
|---|---|---|---|---|---|---|---|
| II-1 | 2.172 | 6.03 | 6.13 | 4.50 | 4.60 | 3.36 | 3.47 |
| I-1 | 2.055 | 6.23 | | 4.69 | | 3.59 | |
| I-3 | 1.828 | 7.30 | 7.07 | 5.30 | 5.30 | 3.36 | 3.37 |
| II-3 | 1.923 | 6.85 | | 5.30 | | 3.38 | |
| II-2 | 2.054 | 8.21 | 8.78 | 6.20 | 6.40 | 3.36 | 3.29 |
| I-2 | 1.940 | 8.67 | | 6.30 | | 3.40 | |
| III-1 | 1.928 | 9.47 | | 6.72 | | 3.11 | |
| II-5 | 1.706 | 16.19 | 16.75 | 11.72 | 11.82 | 3.09 | 3.06 |
| I-5 | 1.593 | 17.31 | | 11.92 | | 3.02 | |

Lind and Truesdale, experiments at 37°, by titration

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 0.78 | 71.1 | 72.3 | 32.0 | 30.2 | 2.64 | 2.55 |
| 2 | .80 | 73.6 | | 28.4 | | 2.48 | |

TABLE IX

TEMPERATURE COEFFICIENT OF HYDROGEN SULFIDE DECOMPOSITION

| | Actual values $M_{H_2S}/N_{H_2S}$ from graph, $t$, °C. | | | Ratio $M_{H_2S}/N_{H_2S}$ at $t$, °C. to $M_{H_2S}/N_{H_2S}$ at room temp. | | |
|---|---|---|---|---|---|---|
| , °C. | 5% $H_2S$ decomp. | 10% $H_2S$ decomp. | 25% $H_2S$ decomp. | 5% $H_2S$ decomp. | 10% $H_2S$ decomp. | 25% $H_2S$ decomp. |
| 37 | 3.40 | 3.12 | 2.66 | 1.0 | 1.0 | 1.0 |
| 200 | 3.22 | 2.91 | 2.42 | 0.95 | 0.93 | 0.91 |
| 234 | 2.85 | 2.47 | 1.83 | .84 | .79 | .68 |
| 270 | 2.58 | 2.20 | 1.56 | .76 | .71 | .59 |

**Effect of Temperature Increase on $M/N$ Values.**—The same procedure was then followed with the results obtained in the present experiments at 200, 234 and 270° (one of Wourtzel's values at 220° seemed to coincide well with the newer values at 200°), the Curves II, III and IV being obtained at these respective temperatures, in Figs. 3 and 4. Although

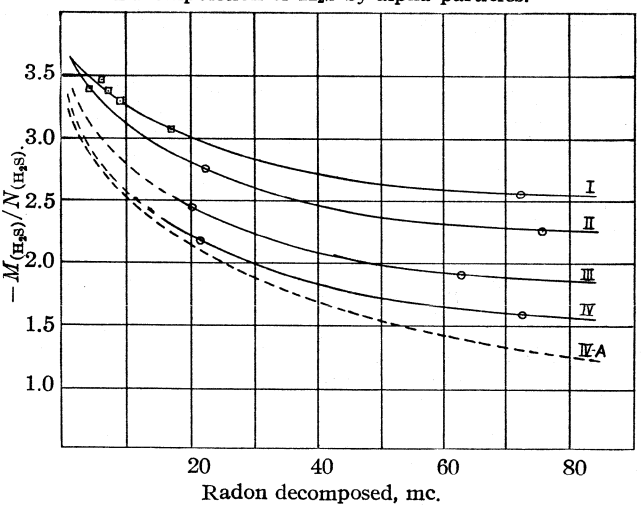


Fig. 3.—$M/N$ as a function of radon decomposed: ⊡, recalculated values of Wourtzel; ⊙, present values.

there are hardly sufficient points on each curve to make it accurate, one may safely be guided by analogy to the curve obtained at room temperature. It seems logical to suppose that the initial $M/N$ value is about the same at all these temperatures. By plotting the results in this way the effect of increasing the temperature becomes evident at once, as interpreted by reference to the results already obtained in the synthesis of hydrogen sulfide. At 200° the thermal synthesis of hydrogen sulfide is just barely measurable, and in extended experiments of several days' duration would cut down the net decomposition of hydrogen sulfide slightly. At 234° this thermal synthesis would be more than twice as great as at

200°, while at 270° we must consider that synthesis of hydrogen sulfide is occurring thermally both on the wall and in the gas phase. The fact that Curve IV does not then lie lower down than is the case may be explained both by the fact that this experiment was of shorter duration than the others in which comparable amounts of reaction occurred (1,2,3,6), and by an additional factor which will be referred to in the next section. The broken Curve IV-A indicates what one might expect if the duration of the experiment had been of the usual length.

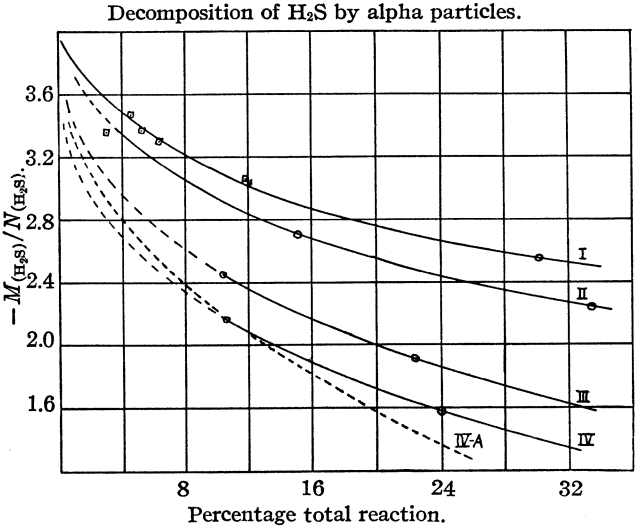


Fig. 4.—$M/N$ as a function of extent of reaction: ⊡, recalculated values of Wourtzel; ⊙, present values.

We may now obtain a temperature coefficient for the $M/N$ values. Wourtzel originally reported that the value of the $M/N$ ratio was 0.90 at 95° and 0.70 at 220° of the value obtained at 18° (2.5 by his method of calculation). Accurate values of the temperature coefficient may be obtained only by comparing $M/N$ values from gas mixtures of the same composition, and this was done by dividing the $M/N$ value at a given percentage reaction on each of Curves II, III and IV, Fig. 4, by the $M/N$ value at the same percentage reaction, from Curve I. These comparisons are indicated in Table IX at 5% (approximately in the range of Wourtzel's experiments) and also at 10 and 25% decomposition. It is seen that these ratios are of the same order of magnitude as those reported by Wourtzel.

**Correction of $M/N$ Values for Back Reaction.**—If synthesis of hydrogen sulfide is the sole cause of the decrease in $M/N$ with extent of reaction, then by calculating the amount of this correction we should be able to

obtain a true $M/N$ value which is independent of both temperature and extent of reaction. Such calculations were made for Experiment 1 at 37°, Experiment 3 at 200° and Experiment 7 at 270°, in the following manner. At 37° there is no thermal synthesis and the only correction is for the synthesis due to ionization of hydrogen and sulfur. Using an average pressure of hydrogen corresponding to that calculated for hydrogen sulfide, and assuming (as an extreme condition) that there is no exchange ionization, $N$, the number of ion pairs formed on hydrogen was obtained. Then taking $M/N$ for synthesis as 0.053 (see Expt. 10, Table IV) since the surface of the bulb was covered with a deposit of sulfur formed by the decomposition of hydrogen sulfide ($+M_{H_2S}$), the number of molecules of hydrogen sulfide synthesized, was calculated. This number, added to ($-M_{H_2S}$) the number of molecules of hydrogen sulfide decomposed from experiment, gave the number of molecules actually decomposed in the course of the experiment. Similar calculations were made in Experiments 3 and 7, using a theoretical $M/N$ for synthesis of 2.0 and 3.0, respectively, again to establish the most favorable case. In addition it was necessary to obtain the number of molecules of hydrogen sulfide obtained thermally, ($+M_t$), and the sum of ($+M_{H_2S}$), ($-M_{H_2S}$) and ($+M_t$) gave the number of molecules of hydrogen sulfide which would have been found to be decomposed had there been no back reaction. For each case this total was divided by the respective $N$ as originally calculated, giving a new value of $M/N$ which should have approached the (arbitrary) initial $M/N$ of 3.75. Errors due to such calculations are chiefly two: (1) if $M$ is assumed to increase then $N$ should decrease very slightly due to the change in composition, and (2) the thermal synthesis at 270° could be estimated only approximately.

The results thus obtained at first seemed surprising, but were readily explained. At 37° the back reaction as calculated was about 1/125 as large as it should be to account for the drop in $M/N$ from 3.75 to 2.6. At 200° the calculated back reaction was about one-fourth as great as it should be, while at 270° the calculated back reaction was approximately of the desired magnitude. Thus if we are to maintain the original explanation for low $M/N$ values, it must be admitted that at 37° the *synthesis* of hydrogen sulfide by ionization in a bulb in which hydrogen sulfide is being decomposed is 125 times as efficient as in a bulb in which synthesis *only* is occurring, that at 200° such synthesis is four times as efficient, and that at 270° the efficiency of the synthesis of hydrogen sulfide is the same whether or not there is a simultaneous decomposition of this gas. The explanation of such a peculiar condition is the following. At 37° sulfur has such a low vapor pressure that it would normally be found almost entirely on the wall of the bulb. In these experiments it can be formed by alpha particle decomposition of hydrogen sulfide faster than it can reach the walls and

come into thermal equilibrium. Hence there will be an excess of sulfur atoms, molecules and larger aggregates in the vapor phase, and this excess is subject to reaction with hydrogen ions and in fact will also receive its share of ionization by alpha particles, thus promoting the synthesis of hydrogen sulfide at a rate very much faster than would be the case if thermal equilibrium were maintained. At 200° the vapor pressure of sulfur is at least 1000-fold greater, hence such an effect would be less marked, while at 270° the amount of sulfur formed per second would be a negligible fraction of the equilibrium concentration and at this temperature thermal equilibrium would be established much more rapidly.

In support of this argument it may be emphasized that during the decomposition of hydrogen sulfide at 37° a "fog" of sulfur particles was always visible in the bulb, sulfur being slowly deposited on the lower surface of the bulb. In addition there must also have been present many smaller, invisible aggregates. A simple calculation shows that the concentration of sulfur present in thermal equilibrium at 37, 200 and 270° is $3.14 \times 10^{12}$, $6.6 \times 10^{16}$ and $1.5 \times 10^{18}$ molecules per cc. Using the data of Experiment 2, assuming 75 millicuries of radon to be undergoing decomposition and assuming an $M/N$ value of 4, it is found that there would be produced about $2.6 \times 10^{13}$ atoms of sulfur *per second* per cc., or assuming eventual formation of $S_8$ there would be formed $3.25 \times 10^{12}$ molecules of sulfur per second per cc. Thus at 37° there were obtained as many molecules of sulfur per second per cc. as there should be in thermal equilibrium with the sulfur on the wall. Since sulfur continues to be formed at this rate it is easy to see that the concentration in the gas phase soon becomes enormously greater than that required by the condition of thermal equilibrium.

**$M/N$ as a Function of Intensity of Ionization.**—The data on the decomposition of hydrogen sulfide are not suited to a comparison of $M/N$ values as related to intensity of ionization. The experiments were not planned to test this point, since in a one-component system at a pressure of one atmosphere it seems reasonable to believe that, with any ordinary intensity of ionization, there should always be a sufficient concentration of reactant molecules to partake with maximum efficiency in whatever reactions follow the initial act of ionization.

**Mechanism of the Decomposition of Hydrogen Sulfide.**—It has been shown that as the decomposition of hydrogen sulfide proceeds under the influence of alpha particle ionization, instead of maintaining a two-phase system in approximate thermal equilibrium, we have present a large excess of sulfur vapor and a fairly high concentration of suspended sulfur particles. This condition speeds up both the thermal and ionized back reaction so that, at least below 270°, such back reaction cannot be correctly estimated. Moreover, it is not known what role this excess sulfur may

play in influencing the main reaction. It therefore seems doubtful whether one could hope to set up a satisfactory kinetic equation from which information could be obtained concerning the mechanism of the decomposition reaction at temperatures below 270°, and at higher temperatures the thermal synthesis of hydrogen sulfide would be so great as to interfere seriously.

The three pieces of evidence upon which a reasonable guess as to the mechanism of the decomposition reaction depends are (1) that the initial $M/N$ value is nearly 4.0, (2) that this *initial* $M/N$ is probably independent of temperature and (3) that the value of $M/N$ is independent of pressure from 0.8 to 12 atmospheres. If we assume that the decomposition of hydrogen sulfide is the result of a reaction between positive ions and electrons, or between positive and negative molecular ions either single or clustered, we should expect the second and third of the above conditions to hold. In order to account for the $M/N$ value of 4 it would probably be sufficient to assume that ion clustering occurred, for otherwise it would be necessary to assume what amounts to a chain mechanism, which should be dependent on temperature and pressure.

## Summary

**The Synthesis of Hydrogen Sulfide.**—1. The synthesis of hydrogen sulfide by alpha particle ionization has been studied at temperatures from 37 to 270°, the value of $(+M_{H_2S}/N_{H_2+S})$ for this reaction varying from 0.021 to 1.48 in this interval, the chief function of temperature increase being to increase the vapor pressure of sulfur to a point where efficient synthesis can proceed. Above 234° there is a pronounced temperature coefficient for the $M/N$ values due to the increased efficiency of the chemical steps involved in the synthesis.

2. Decrease of $M/N$ values with increased extent of reaction cannot be accounted for entirely on the basis of normal back reaction, but is related to the intensity of ionization, perhaps through the medium of exchange ionization.

3. The mechanism of the formation of hydrogen sulfide in an ionized system is complex, and seems to be due to a simultaneous reaction between positive hydrogen ions and negative sulfur ions, between sulfur atoms and hydrogen molecules and between hydrogen atoms and sulfur molecules.

**The Decomposition of Hydrogen Sulfide.**—1. The decomposition of hydrogen sulfide has been studied at four temperatures from 37 to 270°, the maximum value of $(-M_{H_2S}/N_{H_2S})$ being nearly 4.

2. The occurrence of a temperature coefficient less than unity for this reaction, first reported by Wourtzel, has been verified. The true $M/N$ value for this reaction is probably independent of temperature; but a

thermal synthesis together with an abnormally large synthesis of hydrogen sulfide by ionization, gives rise to an effective $M/N$ which decreases with increasing temperature.

3. The ion cluster mechanism accounts satisfactorily for the observed characteristics of the decomposition reaction (neglecting back reaction), though it is not necessary to insist upon this as the only possible mechanism.

4. The fact that the decomposition of hydrogen sulfide by alpha particle ionization is more efficient than its synthesis is probably due to the fact that the vapor pressure of sulfur is so small at the temperatures employed, thus limiting the efficiency with which the ionization energy may be utilized in the synthesis of hydrogen sulfide.

MINNEAPOLIS, MINNESOTA

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

# THE CATALYTIC DECOMPOSITION OF AZOMETHANE, SYM.-DIMETHYLHYDRAZINE, AND MONOMETHYLAMINE: THE THERMAL DECOMPOSITION OF SYM.-DIMETHYLHYDRAZINE

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A study of the catalytic decomposition of azomethane was undertaken for the two-fold purpose of learning more of the influence of catalysts upon various C–N linkages and of ascertaining whether the first order homogeneous gaseous reaction could be accelerated by the presence of proper catalysts. It soon became apparent, however, that the final products of the catalytic reaction were principally ammonia, hydrogen and carbon, rather than nitrogen and ethane, which Ramsperger[1] has shown are produced by the thermal homogeneous decomposition

$$CH_3N{=}NCH_3 \longrightarrow C_2H_6 + N_2 \qquad (1)$$

Nevertheless, the catalytic studies were continued with a view to elucidating the steps by which compounds such as azomethane decompose over catalytic materials. In the course of the azomethane studies it became desirable to investigate also the catalytic decomposition of dimethylhydrazine and monomethylamine, and the thermal decomposition of dimethylhydrazine.

## Experimental

The catalytic and thermal decompositions were carried out in a static system. The reaction vessel was kept at any constant temperature between 220 and 350° by a surrounding mercury vapor bath, the pressure of

[1] Ramsperger, THIS JOURNAL, **49**, 912, 1495 (1927); **51**, 2134 (1929).

which was automatically regulated. The catalyst either as a gauze or in the form of 8–14 mesh particles supported in a platinum basket could be inserted into or removed from the reaction vessel magnetically. A mercury manometer and Toepler pump connected to the reaction vessel completed the essential parts of the apparatus.

The arrangement for inserting and removing the catalyst from the reaction vessel resulted in about 10–15% of the reacting gas being in side tubes at room temperature rather than at the temperature of the reaction vessel. In the experiments on the non-catalytic decomposition of dimethylhydrazine the catalyst tube itself was sealed off, leaving only the side tubes and traps which together contained 7–8% of the reacting gas.

The silver and platinum gauzes used as catalysts were 80 mesh and had an actual surface area of about 80 sq. cm. The iron catalyst used for most of the runs was a doubly promoted synthetic ammonia catalyst containing about 0.25% $K_2O$, and 1.05% $Al_2O_3$, and weighing 1.15 g. as oxide; it was reduced in hydrogen at 500°. In one experiment on dimethylhydrazine a pure iron wire having a surface area of 73 sq. cm. was used.

In each experiment the reaction vessel was filled to about 50 mm. with the gas to be studied. Pressure changes were followed manometrically from the instant at which the catalyst was lowered into the reaction vessel. When desired, the manometer could be lowered and samples of the gaseous mixture pumped out of the system by a Toepler pump and analyzed. Analyses of the gaseous products were carried out in a Bone and Wheeler gas analysis apparatus; hydrogen was determined by removing it with hot copper oxide, and the methane and ethane by combustion over a hot platinum wire in the presence of excess oxygen.

Both the azomethane and the dimethylhydrazine were made from dimethylhydrazine hydrochloride prepared by the method given by Thiele[2] and supplemented by Ramsperger.[1] The azomethane was formed by oxidizing dimethylhydrazine dihydrochloride with potassium chromate, while the dimethylhydrazine was prepared by dropping water on a mixture of dimethylhydrazine dihydrochloride and sodium hydroxide. The gases were dried thoroughly over soda lime; they were then condensed in a solid carbon dioxide–acetone bath and pumped free of ammonia and dissolved air. Azomethane was stored as a gas. Dimethylhydrazine has a boiling point of 81°; an approximate vapor pressure determination indicated the boiling points of the supply used in the present experiments to be 82.5 ± 2°. The methylamine was prepared by dropping 30% monomethylammonium hydroxide on soda lime, condensing the evolved gas in a solid carbon dioxide trap and drying the product finally by passage through a soda lime tube.

[2] Thiele, *Ber.*, **42**, 2576 (1909).

## Results

(a) **The Catalytic Decomposition of Azomethane.**—Negative results were obtained with both silver and platinum gauzes both before and after their activation by treatment with a hydrogen–oxygen mixture. The catalysts could be removed or inserted at will without influencing to any detectable amount the rate of decomposition at 280°. The rate curves of the homogeneous decomposition for initial pressure of about 50 mm. of azomethane are those of a first order reaction. The approximate constants calculated at 280° are, on an average, about 0.046, in good agreement with 0.052, obtained by Ramsperger at the same temperature and pressure.

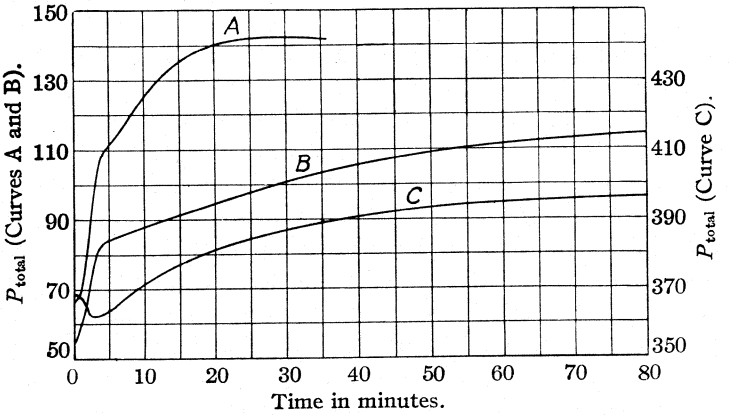


Fig. 1.—Catalytic decomposition of azomethane on iron synthetic ammonia catalysts: Curve A, azomethane at 280°; Curve B, azomethane at 250°; Curve C, azomethane + 310 mm. of hydrogen at 250°.

In the presence of an iron synthetic ammonia catalyst azomethane decomposes rapidly. Pressure changes during typical runs are illustrated by curves A and B in Fig. 1, for 280 and 250°, respectively. A rapid pressure increase equal to about 50% of the initial pressure occurs in the first five minutes; this is followed by a much slower increase, the final pressure being approximately 2.20 times the initial pressure of azomethane.

Analysis of the products of reaction showed that at the end of the catalytic runs the principal gaseous products were ammonia and hydrogen. In addition, small quantities of methane, ethane and nitrogen were present. In Table I are shown the partial pressures of each of the various products present at the end of typical runs. In some of the runs the catalyst was removed at the end of the first five minutes and the products analyzed. As can be seen by comparing runs 23 and 36 with 9, 11, 34 and 38, the principal change occurring after the first five minutes in the catalytic runs results in an increase in the partial pressure of water-soluble material and the partial pressure of hydrogen. At the end of the first five minutes prac-

tically all of the azomethane had disappeared. This was evidenced by the fact that on heating all of the gaseous products at the end of the first five minutes to 360° for an hour, no appreciable pressure increase resulted. Runs 35 and 37 were of this type.

In the course of the work it was noticed that all of the nitrogen was not being accounted for by the products formed. It seemed probable that some nitride might have been formed on the iron catalyst. Accordingly, beginning with run 37, the iron catalyst was analyzed for nitrogen at the end of each run by admitting hydrogen, reducing the nitride to form ammonia, and noting the decrease in pressure resulting. It is apparent from runs 37 and 38 that nearly all of the nitrogen of the original azomethane is accounted for by the summation of that in the nitride and that in the gaseous products. The water-soluble product present at the end of the catalytic runs was principally ammonia; this was deduced from a comparison of the vapor pressure curve of the product, curve A,[3] Fig. 2, with that of ammonia, curve D, Fig. 2.

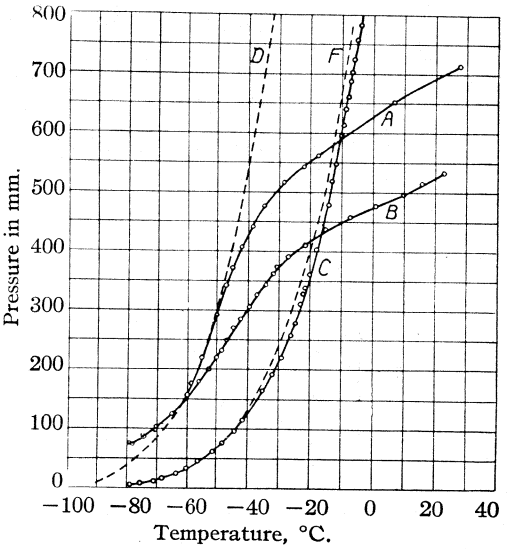


Fig. 2.—Vapor pressure determination of water-soluble constituents.

In a few experiments sufficient hydrogen was added initially to prevent the formation of any iron nitride. In such experiments as shown by curve C, Fig. 1, a pressure decrease occurred during the first five minutes followed by a long gradual increase. At the end of these runs, no nitride was present on the iron catalyst. The pressure decrease is presumably, therefore, associated with the reduction of the iron nitride by the excess hydrogen to form ammonia.

**(b) Thermal Decomposition of Sym.-dimethylhydrazine.**—In determining the thermal behavior of dimethylhydrazine, some approximate data were obtained on its decomposition at 320 and 250°. In Table II are shown the times for one-eighth, one-fourth and one-half decomposition,

[3] It should be noted that curves A and B, Fig. 2, are, strictly speaking, vapor-pressure curves over only those portions lying below about −50 and −30°, respectively. The upper parts of these curves represent a region in which because of the small quantity of material used, the liquid phase was not present. Curves D and F were plotted from data in the "International Critical Tables."

## TABLE I

### RESULTS OF EXPERIMENTS

| | Catalytic azomethane decomposition, 250° | | | | | | | | Dimethylhydrazine decomposition | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | To completion | | | | To "break" | | To "break," catalytically. Then thermally to 350° | | Catalytic to completion, 250° | | Catalytic to "break," 220° | | Catalytic to "break"—250°. Then thermal to 350° | | Thermal, 350° | | Catalytic decomposition of monomethylamine at 250° |
| Run number | 9 | 11 | 34 | 38 | 23 | 36 | 35 | 37 | 46 | 63 | 59 | 58 | 69 | 45 | 49 | 70 |
| Duration of catalyst run, minutes | 135 | 130 | 125 | 182 | 15 | 6 | 5 | 10 | 575 | 665 | 43 | 14 | 13 | 177 | 354 | 120 |
| Initial pressure of reactant, mm. | 47.5 | 47.0 | 55 | 53.0 | 97.0 | 52.5 | 54 | 51.5 | 52.0 | 52.5 | 51.5 | 53.5 | 50.0 | 72.0 | 49.0 | 77.5 |
| Pressure after removing catalyst, mm. | ... | ... | ... | ... | ... | .. | 79.0 | 71.5 | ... | ... | .. | 80.0 | 73.0 | ... | ... | ... |
| Final pressure, mm. | 104.5 | 102.5 | 117.5 | 104.5 | 128.5 | 77.0 | 82.0 | 73.0 | 158.5 | 149.0 | 76.5 | 96.0 | 86.5 | 172.0 | 114.0 | 151.5 |
| Mm. of water-soluble product | 54.3 | 56.3 | 57.7 | 60.5 | 75.5 | 42.3 | 35.8 | 38.2 | 83.2 | 81.2 | 63.2 | 51.8 | 48.6 | 29.2 | 20.3 | 73.7 |
| Mm. of ammonia from $Fe_4N$ | ... | ... | ... | 41.0 | ... | .. | .. | 45.0 | 7.0 | ... | ... | .. | 8.0 | ... | ... | 5.0 |
| Mm. of hydrogen | 34.1 | 38.2 | 41.9 | 26.9 | 46.3 | 19.5 | 19.8 | 15.0 | 60.0 | 47.5 | 0.2 | 0.2 | 0.9 | 0.0 | 0.0 | 73.3 |
| Mm. of methane | 9.4 | 7.6 | 10.9 | 12.0 | 2.1 | 4.8 | 15.8 | 11.6 | 3.5 | 6.0 | 5.4 | 18.4 | 19.8 | 66.0 | 45.7 | ... |
| Mm. of ethane | 4.8 | 1.3 | 1.9 | 2.3 | 4.0 | 4.2 | 2.2 | 2.9 | 4.3 | 3.1 | 0.8 | 3.6 | 1.7 | 17.6 | 8.7 | 1.7 |
| Mm. of unsaturated hydrocarbons | ... | ... | ... | 0.0 | ... | 0.8 | 1.9 | 2.0 | ... | ... | .. | .. | .. | 0.0 | ... | ... |
| Mm. of nitrogen (by difference) | 1.8 | 0.0 | 5.2 | 2.8 | 0.6 | 5.4 | 6.6 | 3.4 | 7.7 | 11.2 | 7.0 | 22.0 | 15.5 | 59.2 | 39.3 | 2.8 |
| Percentage of nitrogen accounted for assuming one nitrogen atom per mole of water-soluble product: (a) neglecting $Fe_4N$ | 60.9 | 59.8 | 61.8 | 62.3 | 64.8 | 50.5 | 45.0 | 43.8 | 94.8 | 98.7 | 75.0 | 89.5 | 79.7 | ... | ... | ... |
| Percentage of nitrogen accounted for assuming one nitrogen atom per mole of water-soluble product: (b) including $Fe_4N$ | ... | ... | ... | 100.0 | ... | .. | .. | 87.5 | 102.0 | ... | .. | .. | 87.6 | 103.0 | 101.0 | ... |
| Percentage of hydrogen accounted for: (a) Water-soluble (calculated as $NH_3$) | 104.0 | 100.0 | 95.4 | 93.4 | 60.3 | 67.8 | 71.2 | 70.0 | 98.4 | 90.8 | .. | .. | .. | 79.5 | 75.4 | ... |
| Percentage of hydrogen accounted for: (b) Water-soluble as $CH_3NH_2$ | ... | ... | ... | ... | 86.3 | 94.8 | 93.2 | 94.7 | ... | ... | 83.2 | 83.0 | 78.8 | 89.3 | 86.0 | ... |

as well as the values of the first order constant $k_1$, calculated for successive two-minute intervals by the formula

$$k_1 = \frac{2.303}{t_2 - t_1} \log_{10} \frac{P_1}{P_2}$$

and expressed as reciprocal seconds. Runs 54 and 55 were made with the reaction vessel packed with fire-glazed Pyrex tubes sufficient to increase the surface to volume ratio about five-fold. The calculated first order constants were reasonably constant between about 15 and 80% decomposition in all runs except 55, where for some unknown reasons the constants increased steadily to a maximum and then decreased. The values of the constants for percentage decompositions less than 15% and greater than 80% were smaller than those in the interval 15–80%. The average value 1.97 for run 55 was taken over the range 20–80% decomposition. The change in reaction rate with temperature shown in Table II corresponds to an energy of activation of about 57,000 calories per mole.

The products of the thermal decomposition indicated a very complex reaction. They were principally methane and nitrogen, together with considerable quantities of ethane, and of some water-soluble material. A vapor pressure determination on this water-soluble material as represented by curve B, Fig. 2, is rather inconclusive, apparently indicating, however, the presence of both ammonia and monomethylamine. The analyses of runs 45 and 49 shown in Table I illustrate the relative amounts of the various products formed.

The data shown in Table II are considered to indicate that the thermal decomposition of dimethylhydrazine is a homogeneous first order reaction. However, because the reaction vessel contained, as already pointed out, only 92% or so of the gas in the reaction system, and because runs at only a limited number of pressures and temperature were taken, these conclusions must be regarded as tentative. Because of the apparently complex nature of the thermal decomposition, further experiments were not carried out.

TABLE II

RATE OF THERMAL DECOMPOSITION ON DIMETHYLHYDRAZINE

| Run | $T$, °C. | Initial pressure, mm. | Ratio of final to initial pressure | Time (minutes) for fractional decomposition 1/3 | 1/4 | 1/2 | $k_1 \times 10^3$ (seconds)$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 45 | 350 | 72 | 2.42 | 3.5 | 6.0 | 11.5 | 1.31 |
| 49 | 350 | 49 | 2.42 | 3.0 | 5.2 | 10 | 1.39 |
| 50 | 350 | 22 | 2.69 | 3.2 | 6.0 | 12.5 | 1.04 |
| 54[a] | 350 | 45.5 | 2.27 | 3.3 | 6.0 | 12.5 | 1.04 |
| 55[a] | 350 | 58.5 | 2.24 | 4.0 | 6.5 | 10.8 | 1.97 |
| 51 | 320 | 56 | 2.37 | 31.5 | 56 | 105 | 0.130 |

[a] In runs 54 and 55 the surface and volume ratio was increased about five-fold by packing the reaction vessel with glass rods.

(c) **The Catalytic Decomposition of Dimethylhydrazine.**—The catalytic decomposition of dimethylhydrazine over iron catalysts at 250° is illustrated by curve A in Fig. 3. The curve is similar to those for the catalytic decomposition of azomethane since it indicates a rapid 50% pressure increase in the first few minutes followed by a much slower pressure increase for several hours.

The final products of the catalytic decomposition are ammonia and hydrogen, principally, with small percentages of ethane, nitrogen and methane. Typical analyses are shown in Table I for runs 46 and 63.

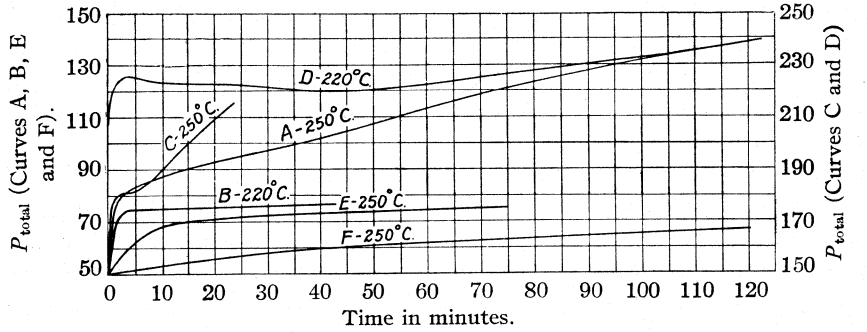


Fig. 3.—Catalytic decomposition of dimethylhydrazine: Curves A and B, pure dimethylhydrazine; Curves C and D, dimethylhydrazine + excess hydrogen; Curve E, dimethylhydrazine with iron wire catalyst; Curve F, dimethylhydrazine with platinum gauze catalyst.

In order to study more fully the reactions occurring during the catalytic processes, some decomposition experiments were carried out at 220°. The initial rapid reaction was found to occur as at 250°, in about two or three minutes, giving again a 50% pressure increase. The slower subsequent decomposition occurring at 250° was, however, practically entirely absent at 220°. A typical rate curve is shown in Fig. 3, curve B.

Analysis of the products of the reaction at 220° showed principally a water-soluble product together with smaller quantities of nitrogen and methane and a trace of ethane. The water-soluble constituent present was definitely identified as monomethylamine. Its vapor pressure curve is shown by curve C, Fig. 2, compared to that of pure monomethylamine in curve F. Run 59, Table I, illustrates the composition of the final products. When these were heated thermally to 350°, a decrease occurred in the partial pressure of water-soluble material and an increase in methane, nitrogen and ethane, as well as in the total pressure. This change in composition can probably be attributed to the decomposition of some dimethylhydrazine, diffusing out of some of the side tubes of the reaction vessel, since the latter as already pointed out was so designed for the catalytic work as to leave about 15% of its contents outside the heated zone.

In two runs excess hydrogen was added initially. The influence on the rate is shown by curves C and D in Fig. 3. In the presence of the excess hydrogen the initial pressure rise in the first two minutes was followed by a slight decrease and then a final increase that was definitely faster than in the absence of the excess hydrogen.

At the completion of the catalytic runs on the decomposition of dimethylhydrazine over iron synthetic ammonia catalysts, the activities of the iron wire catalyst and of a platinum gauze were determined. The rates of decomposition over these catalysts at 250° are shown in Fig. 3, curves E and F. The rate over platinum was sufficiently small to have warranted its being neglected in the work with synthetic ammonia catalysts supported in platinum baskets. The nature of the curve on unactivated iron wire suggests that the same qualitative type of decomposition is occurring at a rate considerably slower than on the active catalyst. The initial rapid pressure rise represents an increase of only about 35% instead of 50% in pressure. No analyses of the products of these two runs were made.

(d) **Catalytic Decomposition of Monomethylamine.**—Several experiments on the decomposition of monomethylamine over iron synthetic ammonia catalysts were carried out at 250°. The rate of decomposition is similar to that occurring after the first few minutes in the decomposition runs on both azomethane and dimethylhydrazine. The analysis of the final products formed in run 70 is shown in Table I. The monomethylamine apparently decomposed practically quantitatively into ammonia, hydrogen and carbon. Monomethylamine was found to be stable in a Pyrex vessel at 350° in the absence of a catalyst.

## Discussion and Conclusions

In the present experiments it has not been found possible by either silver, platinum or iron catalysts to catalyze the decomposition of azomethane into nitrogen and ethane according to equation (1) above. It is true, of course, that in all catalytic azomethane runs over iron catalysts both nitrogen and ethane were produced in quantities larger than would have been produced thermally at the same temperature. However, the catalytic reaction was so complex a process that the small quantities of both nitrogen and ethane might easily have been formed by some side reactions rather than by the speeding up of reaction (1).

The decomposition of azomethane by iron catalysts into ammonia, carbon and hydrogen can be explained by the successive reactions

$$8Fe + 2CH_3NNCH_3 = 2CH_3NH_2 + H_2 + 2Fe_4N + 2C \quad (2)$$

$$CH_3NH_2 = NH_3 + H_2 + C \quad (3)$$

$$2Fe_4N + 3H_2 = 2NH_3 + 8Fe \quad (4)$$

Reaction (2) occurs rapidly, accounting for the rapid pressure increase during the first five minutes and is followed by reactions (3) and (4) which

proceed somewhat more slowly and are responsible for the more gradual increase in pressure extending over a period of several hours. The production of small quantities of methane, ethane and nitrogen in addition to the primary products ammonia, carbon and hydrogen occurs by some side reactions the nature of which is not known. The occurrence of Reactions 2, 3 and 4 has been deduced from and is consistent with the following observations, most of which have been mentioned in connection with the experimental results: (1) a pressure increase of about 50% occurs within the first five minutes. (2) At the completion of this rapid initial pressure rise, no azomethane remains undecomposed. (3) The final gaseous products at the end of the catalytic runs are principally hydrogen and ammonia in addition to small quantities of methane, ethane and nitrogen. (4) Methylamine is thermally stable at 350° in the absence of a catalyst; in the presence of iron synthetic ammonia catalysts at 250° it decomposes at a rate that is in good agreement with that obtained in the last slow pressure increase of the catalytic azomethane runs. (5) The assumption that the water-soluble product formed during the first five minutes of the catalytic azomethane decomposition is monomethylamine accounts for about 95% of the hydrogen present in the original sample compared to 70% that would be accounted for by assuming this product to be ammonia. (6) During the portion of the catalytic run occurring after the first five minutes, the partial pressures of both the water-soluble material and of hydrogen increase. (7) The presence of an excess of hydrogen in the original reaction mixture prevents the initial, rapid, 50% pressure increase from occurring. It is apparent that if reactions (2) and (4) are added in such a way as to eliminate the formation of iron nitride, the resulting equation is for a reaction entailing no volume change. Actually a pressure decrease of from 1 to 12 mm. resulted within the first five minutes during these excess hydrogen runs. The nature of the reaction causing this decrease is uncertain. (8) The final ammonia–hydrogen ratios conform closely to those that would be found at similar pressures in equilibrium with Fe–$Fe_4N$. The agreement of the values of $K = (NH_3)^2/(H_2)_3$ found in the present experiments with the equilibrium curve for the system Fe–$Fe_4N$–$NH_3$–$H_2$[4] extrapolated from 400° down to 250° is shown in Fig. 4.

Between 50 and 75% of the products of the thermal decomposition of dimethylhydrazine can be accounted for by the reaction

$$CH_3NHNHCH_3 = 2CH_4 + N_2 \qquad (5)$$

The excess nitrogen, the water-soluble product, and the ethane formed in the homogeneous decomposition are presumably the results of some side reactions. Possibly the occurrence of short chain reactions between various gaseous radicals such as suggested by F. O. Rice[5] for certain organic

[4] Brunauer, Jefferson, Emmett and Hendricks, THIS JOURNAL, 53, 1778 (1931).

[5] F. O. Rice, *ibid.*, 53, 1959 (1931).

decompositions accounts for the products formed. However, no simple reaction has been devised that will explain the formation of products other than those indicated by reaction (5) above.

The catalytic decomposition of dimethylhydrazine probably resembles closely that of azomethane. The one striking difference is that at the end of the initial rapid pressure rise monomethylamine and methane, but no

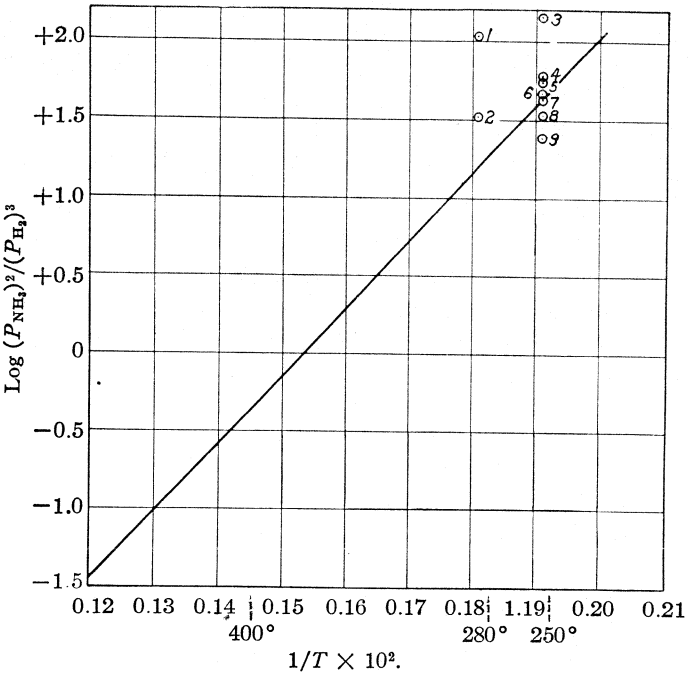


Fig. 4.—Composition of final $NH_3$–$H_2$ mixtures in catalytic azomethane and dimethylhydrazine decomposition over iron catalysts: 1, 2, 3, 4, 5, 7, 8, from azomethane runs; 6, 9, from dimethylhydrazine runs.

free hydrogen, are present in the gaseous products. The analysis of the products at this point agrees fairly well, in fact, with the empirical equation

$$16Fe + 8CH_3NHNHCH_3 = 12CH_3NH_2 + CH_4 + 4Fe_4N + 3C \qquad (6)$$

Reactions (3) and (4) above are presumably responsible for the gradual pressure increase occurring after the first few minutes.

In the presence of excess hydrogen, it might be expected that no $Fe_4N$ would form and that the pressure increases would correspond to the combination of reactions (6) and (4), to give

$$8CH_3NHNHCH_3 + 6H_2 = 12CH_3NH_2 + CH_4 + 4NH_3 + 3C \qquad (7)$$

Run 72, shown as curve C, Fig. 3, made with 56 mm. of dimethylhydrazine

and excess hydrogen seems to be in approximate agreement with equation (7).

The catalytic decomposition of methylamine according to reaction (3) above is particularly interesting in that it demonstrates the ability of nitrogen over iron catalysts at 250° to not only detach itself from a linkage with carbon but to break the C–H bonds, with the formation of ammonia and hydrogen.

No attempt was made to determine definitely the form in which the carbon was deposited on the catalysts used in the various catalytic decompositions.

The authors wish to express their thanks to Dr. W. E. Kuentzel for starting the experimental work and conducting the earlier part of the work on azomethane.

## Summary

Azomethane has been found to decompose rapidly at 250° over iron synthetic ammonia catalysts, the final gaseous products being principally ammonia and hydrogen, with small amounts of methane, ethane and nitrogen. The reaction apparently takes place in two steps, the first resulting in the formation of monomethylamine, hydrogen, $Fe_4N$ and carbon; the second in the decomposition of the monomethylamine and the partial reduction of the $Fe_4N$ by hydrogen. Dimethylhydrazine in a somewhat similar manner decomposes into ammonia, hydrogen and carbon, together with some methane, ethane and nitrogen. Monomethylamine decomposes quantitatively into hydrogen, ammonia and carbon, at 250° on iron catalysts. Dimethylhydrazine has been found to decompose thermally at 320 to 350° as a homogeneous first order gas reaction. It has an energy of activation of about 57,000 calories per mole. About 60% of the products of the homogeneous reaction can be accounted for by the equation $CH_3NHNHCH_3 = 2CH_4 + N_2$. However, considerable amounts of some unidentified water-soluble product, nitrogen and a small amount of ethane not accounted for in the above equation are also formed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

# GERMANIUM. XXXVII. GERMANIUM DIOXIDE GEL. PREPARATION AND PROPERTIES[1]

A. W. LAUBENGAYER AND P. L. BRANDT

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## Introduction

Numerous investigations have shown that silicon dioxide can readily be prepared as a gel by several different methods and that this gel possesses high adsorptive power for the vapors of substances such as benzene, ethyl ether, carbon tetrachloride, water, etc. Important uses for silica gel based upon this property have been described. Since silicon and germanium are members of the fourth group of the periodic table of Mendeléeff and their compounds have been found to possess many properties in common, it seemed worth while to try to prepare a pure germanium dioxide gel and to determine the adsorptive properties of this substance.

Unlike silicon dioxide, germanium dioxide is appreciably soluble in water. Pugh[2] found that 100 g. of water will dissolve 0.447 g. of the oxide at 25°. It is to be expected, therefore, that germanium dioxide will tend to build up crystals and will not form a gel as readily as silica does. Numerous investigators have demonstrated the crystalline nature of the dioxide formed by the ordinary methods. The only record of the formation of a gel was made by van Bemmeln,[3] who passed carbon dioxide through a solution of sodium germanate. This gel, however, adsorbed sodium oxide strongly and after repeated washings with water it still contained one-fifth mole of sodium oxide per mole of germanium dioxide.

It appeared, therefore, that under certain conditions germanium dioxide precipitates as a jelly and under other conditions as a crystalline solid, but the available information was very meager. Accordingly, in this investigation, a preliminary comprehensive study was made of the formation of germanium dioxide, under various conditions.

Hydrolysis of germanium tetrachloride, germanium tetrabromide and germanium tetraiodide by water and by aqueous solutions of the corresponding hydrohalogen acids was investigated at temperatures varying from 0 to 75°, but the product always was crystalline. The same form of precipitate was secured when aqueous solutions of sodium germanate of varying concentration were treated with hydrochloric acid. A gelatinous precipitate was formed when carbon dioxide was bubbled through

[1] This article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Pugh, *J. Chem. Soc.*, 1537–41 (1929).

[3] Van Bemmeln, *Rec. trav. chim.*, **6**, 205 (1887).

0.10 to 0.75 molar aqueous solutions of sodium germanate, but this gel could not be washed free of sodium. Dialysis of an acidified solution of sodium germanate was unsuccessful because the colloidal oxide slowly went into true solution and passed through the membrane. Hydrolysis of germanium tetraethoxyl by water gave a metastable sol which was stabilized by adding alkali. The addition of alkali carbonate to this stabilized sol caused the formation of a gel but it could not be freed of sodium. Methods involving the use of aqueous solutions, therefore, seemed unsuitable for the preparation of such a gel.

Dearing and Reid[4] have prepared silica gel by the action of the calculated amount of water on silicon tetraethoxyl in alcoholic solution and find that a very active product is thus obtained. Applying the method to germanium dioxide the authors found that the use of the proper amounts of germanium tetraethoxyl, ethyl alcohol and water yielded a firm gel, easily freed from alcohol.

## Experimental

**Preparation of Germanium Tetraethoxyl.**—Germanium tetraethoxyl was prepared by the action of sodium ethylate on germanium tetrachloride.[5] The preparation boiled at 187°.

**Formation of Germanium Dioxide Gel.**—Eleven grams of germanium tetraethoxyl was dissolved in 11 cc. of absolute ethyl alcohol (Solution A). This solution was cooled by immersing the container in ice for fifteen minutes; 1.60 g. of water (1.57 g. theoretically required for hydrolysis) was dissolved in 11 cc. of absolute alcohol (Solution B) and this solution also was cooled in ice for fifteen minutes. Solution B was then added to Solution A with very rapid stirring. The mixture set to a gel almost immediately. The test-tube containing this gel was corked and permitted to stand for one hour. Alcohol was then removed from the gel as slowly and uniformly as was possible with so small a sample. It was placed in an uncovered Petri dish in the bottom of a tall beaker, and the beaker was covered with a glass plate so that only the space between the cover and lip was open. The beaker was set in a cupboard at room temperature and under these conditions it took the gel five days to become hard and brittle. The gel was then broken up and placed in a container which could be evacuated by means of an efficient oil pump. The evacuation was carried on for five hours, after which time the gel was heated at 175–180° for four hours while dry air was passed over it. The resulting germanium dioxide was brittle and translucent. The lumps of gel were slightly reddish in color by transmitted light and were bluish-white by reflected light. This method is very satisfactory for preparing pure germanium dioxide gel and material made in this way was used in the following experiments.

**Determination of Adsorptive Power of Germanium Dioxide Gel.**—The adsorptive power of the gel prepared from germanium tetraethoxyl was tested by the method which Holmes, Sullivan and Metcalf[6] used on certain silica gels. Air was passed through a flow-meter and was dried by calcium chloride, concentrated sulfuric acid and phosphorus pentoxide in the order named. The dry air was passed through two Friedrichs gas-washing bottles where it was saturated with the vapor to be adsorbed by the gel.

[4] Dearing and Reid, THIS JOURNAL, **50**, 3058 (1928).

[5] Tabern, Orndorff and Dennis, *ibid.*, **47**, 2039 (1925).

[6] Holmes, Sullivan and Metcalf, *Ind. Eng. Chem.*, **18**, 386 (1926).

The saturated air was led through a spray catcher to remove entrained liquid and was then passed through a tube containing a weighed amount of germanium dioxide gel. The gas-washing bottles, spray-catcher and gel tube were immersed in a thermostat held at 30 ± 0.1°. The air stream was permitted to flow until the gel had reached constant weight.

The values obtained for the adsorption by germanium dioxide gel are given in Table I. For purposes of comparison, corresponding data reported by Holmes, Sullivan and Metcalf[6] for "Patrick's silica gel" and "silica gel from iron" are also included.

TABLE I

GRAMS OF VAPOR ADSORBED PER 100 GRAMS OF GEL

| Vapor adsorbed | Germanium dioxide gel First detn. | Germanium dioxide gel Second detn. | Patrick's silica gel | "Gel from Iron" (silica) |
|---|---|---|---|---|
| Benzene | 47.2 | 47.2 | 32.2 | 62.0 |
| Carbon tetrachloride | 86.3 | 86.6 | 57.7 | 120.0 |
| Ethyl ether | 39.7 | 40.0 | 30.5 | 54.3 |

All of these values for germanium dioxide gel were determined on the same sample, since it was found that the adsorptive capacity of the gel could be restored completely by heating in a stream of dry air at a temperature of 175° for about thirty minutes. The results given in the table show that the adsorbing power of germanium dioxide gel for organic vapors is of the same order as that of silica gel.

Since germanium dioxide is appreciably soluble in water, it seemed worth while to determine the amount of water that could be adsorbed by germanium dioxide gel, and also to find out whether adsorption of water and its subsequent removal from the gel effected any change in the adsorbing power for organic liquids. A new sample of gel was made up by the method described above, except that it was not permitted to stand in a closed tube before removal of alcohol. Apparently this change made some difference in the structure since the sample here obtained adsorbed only 29.1% of its weight of benzene. When regenerated in the manner already described, this sample again showed the same adsorbing capacity for benzene. The lower adsorbing power did not interfere with the experiments, however, since only relative results were desired.

The adsorption of water by this gel was determined in the same manner as has been described for organic liquids. After twenty-eight hours equilibrium had not been reached, but further adsorption of water was very slow; 19.1% of water had been taken up. This water was removed by heating the gel to 200° and passing dry air over it. The adsorbing power of the revivified gel for benzene vapor was found to be 23.0%. Since this value is appreciably lower than the previously determined adsorptive capacity of the sample, it indicates that the gel structure is probably altered in some way by the adsorbed water.

## Summary

1. The physical properties of various preparations of germanium dioxide resulting from the hydrolysis of germanium tetrachloride, tetrabromide, tetraiodide and tetraethoxyl, and from the action of hydrochloric acid and of carbon dioxide on sodium germanate have been investigated.

2. Of the various methods for the preparation of germanium dioxide gel studied, the only procedure that yielded a satisfactory product was the hydrolysis of germanium tetraethoxyl by means of water, the reaction being carried out in alcoholic solution.

3. Germanium dioxide gel was found to possess an adsorptive power for the vapors of benzene, ethyl ether and carbon tetrachloride comparable with that of silica gel.

4. Germanium dioxide gel adsorbs water vapor but upon the removal of the adsorbed water the adsorptive power of the gel for benzene vapor was found to have decreased.

ITHACA, NEW YORK

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

# THE EFFICIENCY OF THE REACTION OH + $H_2$ = $H_2O$ + H AND ITS BEARING ON THE REACTION BETWEEN HYDROGEN AND OXYGEN[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

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The experiments by von Elbe on the photochemical reaction between hydrogen peroxide and hydrogen or carbon monoxide described elsewhere,[4] and a careful estimate, from earlier measurements,[5] of the intensity of incident radiation from the zinc spark, allow one to estimate a limit of the efficiency and the heat of activation of the reaction

$$OH + H_2 = H_2O + H \qquad (1)$$

The total number of quanta entering the reaction vessel per second was $2 \times 10^{15}$. Assuming that the absorption of hydrogen peroxide for the spectral lines used is 30%, calculated from the absorption measurements of Urey, Dawsey and Rice,[6] and a quantum efficiency of $1H_2O_2$ decomposed per quantum absorbed yielding 2OH, the number of OH radicals formed (volume of vessel 86 cc.) was $1.4 \times 10^{13}$ per sec. per cc.

The experimental data show that $5.6 \times 10^{13}$ molecules of hydrogen reacted per second per cc. Thus, practically as many hydrogen molecules disappear per second as hydroxyl radicals are formed per second. The difference between the values $5.6 \times 10^{13}$ and $1.4 \times 10^{13}$ is apparently due primarily to the inaccuracy of the estimated light intensity. We note that the stationary concentration of OH must therefore be smaller or equal to about $5.6 \times 10^{13}$ radicals per cc. In the latter case, the collision frequency between OH and $H_2$ at 40° is $3.9 \times 10^{23}$ per sec. per cc. From these data we can conclude that at least 1 out of $7 \times 10^9$ collisions between OH and $H_2$

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[4] G. von Elbe, THIS JOURNAL, **54**, 821 (1932).

[5] Bernard Lewis, *J. Phys. Chem.*, **32**, 270 (1928).

[6] Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1376 (1929).

succeeds in reacting according to (1). This provides an upper limit for the heat of activation—namely, 14,100 calories. Frankenburger and Klinkhardt[7] calculate a lower limit of 13,500 calories from experiments on the reaction between hydrogen and oxygen under the influence of photochemically produced hydrogen atoms. The true heat of activation must therefore lie about these values, or in other words the collision efficiency must be about $10^{-10}$ at 40°.

It will now be shown that all experimental data published thus far regarding reactions of OH radicals which have a bearing on the present considerations are consistent with the above conclusion. Let us consider the other probable ways of removing OH radicals in these experiments.

$$OH + OH + M \text{ (third body)} = H_2O_2 + M \quad (2)$$

$$OH + OH = H_2O + O \quad (3)$$

$$OH + OH = H_2 + O_2 \quad (4)$$

Reaction 4 can be eliminated since its activation energy is too high.[8] The number of triple collisions occurring by Reaction 2 is between $10^{11}$ and $10^{12}$ per second per cc. (The third body is hydrogen at a pressure of about one atmosphere.) Since the OH concentration is $10^{13}$, then only about $1/100$ to $1/10$ of these OH radicals can disappear per second per cc. by triple collisions, assuming that each triple collision forms hydrogen peroxide.

In Frankenburger and Klinkhardt's experiments the dominant reaction was Reaction 2. Indeed they show that in order to explain their results the triple collision must occur more frequently than the reaction

$$OH + H_2 = H_2O + H$$

In our case the reverse is true due to our lower OH concentration. Frankenburger and Klinkhardt's results also show that the number of triple collisions is in excess of the number of successful collisions between two OH radicals. It follows that Reaction 3 is successful less than once in $10^4$ collisions between two OH radicals. On the other hand, Bonhoeffer and Pearson's data indicate that Reaction 3 is successful at least once in $10^4$ collisions between two OH radicals. Since their gases were heated somewhat by the discharge, their limiting efficiency may be less than this value at the temperature of Frankenburger and Klinkhardt's experiments (about 60°). Therefore, it is evident that the two results are consistent.

From the latter result it can be shown that in the experiments under consideration, less than $1/100$ of the OH radicals can be removed by Reaction 3 since the number of such successful collisions is somewhat less than $10^{11}$ per second per cc. This disposes of all reactions of OH radicals except Reaction 1 with hydrogen.

Frankenburger and Klinkhardt's estimate of the length of the chains in the hydrogen–oxygen reaction at 400° by the Bonhoeffer and Haber mechanism

[7] Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **123**, 431 (1931).

[8] Bonhoeffer and Pearson, *Z. physik. Chem.*, **14B**, 1 (1931).

$$H + O_2 + H_2 = H_2O + OH$$
$$OH + H_2 = H_2O + H$$

puts up a strong case for this mechanism. However, some experiments recently published by Pease[9] are very difficult to explain if hydrogen peroxide can be formed only through Reaction 2.

Pease found a considerable yield of hydrogen peroxide on passing a mixture of hydrogen and oxygen through a Pyrex tube at 550°, amounting in some experiments to as much as one molecule of hydrogen peroxide for four molecules of water formed. Reaction 2 cannot be held responsible for this result for the following reason. Reaction 1 has a collision yield of $1.8 \times 10^{-4}$ at 550°. In order for Reaction 2 to be the source of hydrogen peroxide, one of these should take place for every *ca.* $10^4$ collisions of OH with $H_2$, which means that the concentration of OH would have to be of the order of the $H_2$ concentration, namely, *ca.* $10^{19}$ per cc. This is obviously impossible. We are compelled for these reasons to assume with Pease, who experimented in the non-explosive region, that some other mechanism for the formation of hydrogen peroxide must be in operation.

[9] Pease, THIS JOURNAL, **52,** 5106 (1930); **53,** 3188 (1931).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 16]

# ACTIVITY COEFFICIENTS OF SALTS IN ACETIC ACID SOLUTIONS FROM SOLUBILITY MEASUREMENTS

BY RALPH P. SEWARD AND CLEMENT H. HAMBLET

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Measurement of the solubility of salts in the presence of other salts, although complicated by the introduction of a third component, offers the most exact method of measuring changes in the activity coefficients of salts at low concentration in non-aqueous solutions. Previous research in this field includes the work of Williams[1] on methyl alcohol solutions, Hansen and Williams[2] on ethyl alcohol–water mixtures, Kraus and Seward[3] on isopropyl alcohol and acetone, Robinson[4] on acetone and Seward and Schumb[5] on ethyl alcohol. The results of these investigations have been compared in each case with those predicted by the interionic attraction theory of Debye and Hückel.[6] If the observed activity coefficient changes are

[1] Williams, THIS JOURNAL, **51,** 1112 (1929).

[2] Hansen and Williams, *ibid.*, **52,** 2759 (1930).

[3] Kraus and Seward, *J. Phys. Chem.*, **32,** 1294 (1928).

[4] Robinson, *ibid.*, **32,** 1089 (1928).

[5] Seward and Schumb, THIS JOURNAL, **52,** 3962 (1930).

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

plotted against the square root of the ionic strengths of the solutions, curves are obtained which for salts of higher valence type in methyl alcohol and for all salts in the solvents of lower dielectric constant have a markedly greater slope than the limiting slope which the Debye–Hückel theory requires for dilute solutions. To account for this on the basis of the original Debye–Hückel approximation introduction of a negative value for the ion diameter is necessary.

Gronwall, La Mer and Sandved[7] have shown that the complete development of the equations used by Debye and Hückel gives a series of terms of which the original Debye and Hückel approximation is the first. They have calculated values for the higher terms at different concentrations.

These authors as well as La Mer and Parks and Cowperthwaite and La Mer[8] have obtained, using these values, quantitative agreement between the complete equation and the measured activity coefficients of salts of higher valence type in aqueous solutions. Their equation also predicts curves for non-aqueous solutions which are, qualitatively at least, in agreement with the experimental curves if a reasonable positive value for the ion diameter is assumed. Bjerrum,[9] by treating ions within a certain arbitrary distance as undissociated, has developed values for the activity coefficients which also agree in predicting curves with positive deviations from the Debye–Hückel limiting slope for salts of higher valence type and for solutions of low dielectric constant.

Since both the development of Gronwall, La Mer and Sandved and that of Bjerrum predict greater deviations from the Debye–Hückel limiting slope the lower the dielectric constant, assuming a constant ion diameter, the present investigation was undertaken to determine whether agreement with the theory would be found in solvents with dielectric constants less than ten. Glacial acetic acid was selected as the solvent. Measurements of freezing points of acetic acid solutions have been made by Webb,[10] and e. m. f. measurements by Conant and Werner and by Hutchison and Chandlee.[11] These investigators agree in concluding that the Debye–Hückel theory may be applied to the solutions studied if a rather large value for the ion diameter is assumed.

In the present investigation the solubilities of potassium perchlorate in glacial acetic acid in the presence of ammonium perchlorate, sodium nitrate, and sodium bromide and of potassium nitrate in the presence of ammonium chloride and ammonium nitrate have been measured.

[7] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[8] La Mer and Parks, THIS JOURNAL, **53**, 2040 (1931); Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[9] Bjerrum, *Det. Kgl. Danske Videnskab. Selskab, Math-fys. Medd.*, [9] **7**, 1 (1926).

[10] Webb, THIS JOURNAL, **48**, 2266 (1926).

[11] Conant and Werner, *ibid.*, **52**, 4436 (1930); Hutchison and Chandlee, *ibid.*, **53**, 2881 (1931).

## Preparation of Materials

**Acetic Acid.**—"Reagent quality" acid melting at about 15.65° was refluxed for forty hours with acetic anhydride equivalent to 80% of the water calculated to be present. It was then distilled using a Vigreux column arranged so that the hot vapors were in contact only with glass. In this way large quantities of acid were obtained melting from 16.5 to 16.6°. No acid melting lower than 16.5° was used. If water is assumed to be the impurity present,[12] a melting point of 16.5 corresponds to 0.05% water.

After various methods of purification recommended in the literature had been applied to C. P. acetic acid, without entirely satisfactory results, it was decided to employ "reagent" quality acid, fractional distillation of which yielded suitable material.

**Salts.**—The salts used were C. P. salts, further purified by recrystallization and carefully dried before use.

**Determination of Solubilities.**—The method was, in general, that used by Kraus and Seward. To insure equilibrium an excess of the saturating salt was rotated in a large bath with one to two liters of solvent (acetic acid containing various quantities of added salt) for sixteen hours or longer at about 30° and then at 25 ± 0.02° for at least eight hours. After being allowed to stand without removal from the bath for three hours, the clear solution was siphoned off and analyzed. In some cases filtration was necessary.

The concentration of the added salt was calculated from the total weight of acetic acid used and the weight of solid salt added. In calculating concentrations the densities of the pure solvent were used. The value of 1.044 from the "International Critical Tables" for the density of acetic acid at 25° was used. The concentration of the saturating salt was determined by distilling the acetic acid from a known weight of solution and analyzing the residue.

The number of salts whose solubility is of the magnitude desired is very limited. Considerable time was wasted in an attempt to get consistent values for the solubility of sodium iodate. Apparently equilibrium was not reached even in six days of rotation as the values obtained varied from 0.00036 to 0.00060 mole per liter. This seems to agree with the observations of Hill and Donovan[13] on the solubility of iodates in water. Potassium perchlorate was finally chosen although its analytical determination is not so favorable. The measurements on the solubility of potassium nitrate have been included since the e. m. f. and freezing point measurements referred to have been made in this range of concentrations. In the case of potassium perchlorate in the presence of ammonium perchlorate, and also in the case of potassium nitrate in the presence of ammonium chloride and of ammonium nitrate, the solubility of the saturating salt was determined by adding an excess of concentrated sulfuric acid to the residue left after evaporation of the solvent and igniting in a platinum dish, the po-

[12] DeVisser, *Rec. trav. chim.*, **12**, 101 (1893).

[13] Hill and Donovan, THIS JOURNAL, **53**, 934 (1931).

tassium being weighed as potassium sulfate. The solubility of potassium perchlorate in the presence of sodium nitrate and sodium bromide was measured by the cobaltinitrite method using the procedure recommended by Van Rysselberge.[14] Since the composition of the cobaltinitrite precipitate varies with the conditions of precipitation, each series of determinations was accompanied by two or more determinations of a known weight of perchlorate of the same magnitude as that from the solutions being analyzed in order to determine the weight of potassium perchlorate corresponding to a given weight of cobaltinitrate precipitate. Two samples of solution were withdrawn from each bottle to give check analyses except for potassium chlorate in the presence of ammonium perchlorate. Since the solubility was decreased in this case, all of the solution from each bottle was required to give a large enough weight of potassium sulfate to give reasonable accuracy in weighing. The three values for the solubility of potassium perchlorate in pure acetic acid were obtained from three independent saturations.

**Experimental Data.**—The following tables give the solubilities of potassium perchlorate and of potassium nitrate in the presence of varying amounts of added salts in glacial acetic acid at 25°. For comparison with the theory the calculated values of $-\log P_{i_0}/P_i$ and the square roots of the total salt concentrations are included. All concentrations are expressed in moles of salt per liter of solution.

TABLE I

SOLUBILITY OF POTASSIUM PERCHLORATE IN THE PRESENCE OF OTHER SALTS IN GLACIAL ACETIC ACID AT 25°

(a) Added salt sodium nitrate

| Concn. $NaNO_3$ $\times 10^4$ | Concn. $KClO_4$ $\times 10^4$ (anal.) | | | Concn. $KClO_4$ $\times 10^4$ (mean) | $-\frac{1}{2}\log\frac{P_{i_0}}{P_i}$ | $\sqrt{C} \times 10^2$ |
|---|---|---|---|---|---|---|
| 0.00 | 1.98 | 1.93 | 1.95 | 1.95 | 0.000 | 1.40 |
| 1.68 | 2.53 | 2.54 | | 2.53 | .113 | 2.05 |
| 3.46 | 3.05 | 3.05 | | 3.05 | .193 | 2.55 |
| 6.33 | 3.57 | 3.58 | | 3.57 | .263 | 3.14 |
| 10.09 | 4.11 | 4.16 | | 4.13 | .325 | 3.77 |
| 15.50 | 4.82 | 4.85 | | 4.83 | .393 | 4.50 |
| 18.25 | 5.24 | 5.21 | | 5.22 | .427 | 4.84 |

(b) Added salt sodium bromide

| Concn. NaBr $\times 10^4$ | | | | | | |
|---|---|---|---|---|---|---|
| 0.00 | 1.98 | 1.93 | 1.95 | 1.95 | 0.000 | 1.40 |
| 0.78 | 2.36 | 2.36 | 2.34 | 2.35 | .080 | 1.77 |
| 1.20 | 2.71 | 2.70 | | 2.70 | .141 | 1.97 |
| 1.92 | 2.90 | 2.89 | | 2.90 | .170 | 2.19 |
| 2.10 | 2.88 | 2.88 | | 2.88 | .168 | 2.23 |
| 2.78 | 3.15 | 3.10 | 3.04 | 3.10 | .200 | 2.42 |
| 5.90 | 3.76 | 3.85 | | 3.79 | .287 | 3.11 |

[14] Van Rysselberge, *Ind. Eng. Chem., Anal. Ed.*, **3**, 3 (1931).

TABLE I (*Concluded*)

(c) Added salt ammonium perchlorate

| Concn. $NH_4ClO_4$ $\times 10^4$ | | Concn. $KClO_4$ $\times 10^4$ (anal.) | | Concn., $KClO_4$ $\times 10^4$ (mean) | $-\frac{1}{2}\log\frac{P_{i_0}}{P_i}$ | $\sqrt{C} \times 10^2$ |
|---|---|---|---|---|---|---|
| 0.00 | 1.98 | 1.93 | 1.95 | 1.95 | 0.000 | 1.40 |
| 1.98 | 1.94 | | | | .150 | 1.98 |
| 3.16 | 1.76 | | | | .180 | 2.22 |
| 3.78 | 1.90 | | | | .226 | 2.38 |
| 5.09 | 1.71 | | | | .243 | 2.61 |
| 7.65 | 1.55 | | | | .287 | 3.03 |
| 9.83 | 1.55 | | | | .333 | 3.37 |
| 13.06 | 1.39 | | | | .362 | 3.80 |
| 20.93 | 1.41 | | | | .457 | 4.73 |

TABLE II

SOLUBILITY OF POTASSIUM NITRATE IN THE PRESENCE OF OTHER SALTS IN GLACIAL ACETIC ACID AT 25°

(a) Added salt ammonium nitrate

| Concn. $NH_4NO_3$ $\times 10^2$ | | Concn. $KClO_4$ $\times 10^2$ (anal.) | | Concn. $KClO_4$ $\times 10^2$ (mean) | $-\frac{1}{2}\log\frac{P_{i_0}}{P_i}$ | $\sqrt{C}$ |
|---|---|---|---|---|---|---|
| 0.000 | 1.828 | 1.830 | 1.827 | 1.828 | 0.0000 | 0.1352 |
| 0.437 | 1.854 | 1.853 | | 1.853 | .0519 | .1514 |
| 0.740 | 1.899 | 1.897 | | 1.898 | .0877 | .1634 |
| 1.083 | 1.855 | 1.852 | | 1.853 | .1057 | .1714 |
| 1.917 | 1.937 | 1.940 | | 1.938 | .1747 | .1964 |
| 2.542 | 1.955 | 1.965 | | 1.960 | .2107 | .2122 |

(b) Added salt ammonium chloride

| Concn. $NH_4Cl \times 10^2$ | | | | | | |
|---|---|---|---|---|---|---|
| 0.000 | 1.828 | 1.830 | 1.827 | 1.828 | 0.0000 | 0.1352 |
| 0.182 | 2.106 | 2.092 | | 2.099 | .0599 | .1510 |
| 0.364 | 2.196 | 2.183 | | 2.194 | .0791 | .1599 |
| 0.757 | 2.437 | 2.438 | | 2.437 | .1249 | .1787 |
| 1.132 | 2.727 | 2.724 | | 2.725 | .1734 | .1964 |
| 1.221 | 2.804 | 2.791 | | 2.798 | .1847 | .2005 |

## Discussion

The interionic attraction theory leads to an equation relating the value of minus the logarithm of the activity coefficient of the salt to the concentration of the solution. The development of the theory by Debye and Hückel leads to the equation

$$-\log f = \frac{22.6\sqrt{C}}{1 + 1.166 \times 10^8 a\sqrt{C}} \qquad (1)$$

for acetic acid at 25°, where $C$ is the total salt concentration in moles per liter and $a$ the average ion diameter in centimeters. Since all the salts used are uni-univalent, the coefficients involving valence are omitted.

The development by Gronwall, La Mer and Sandved[15] leads to the equation

[15] Ref. 7, page 388 and Table V, page 387.

$$-\log f = \frac{19.4}{10^8 a} \cdot \frac{x}{1+x} - \frac{307.8}{(10^8 a)^3} F_3(x) - \frac{24{,}460}{(10^8 a)^5} F_5(x) \qquad (2)$$

for univalent type salts in acetic acid at 25°, where $x = 1.166 \times 10^8 a \sqrt{C}$, $a$ and $C$ are the same as above, and $F_3(x)$ and $F_5(x)$ are functions of $x$ whose values have been calculated and tabulated by these authors. The first term on the right in Equation 2 has the same value as $-\log f$ in Equation 1. The two equations, therefore, differ by the values of the second and third terms in Equation 2. The term involving change in dielectric constant with salt concentration has been omitted since its value is unknown. Hutchison and Chandlee,[16] however, conclude that, at concentrations somewhat larger than those of the perchlorate solutions in the present investigation, the effect of this term is less than 1% of the value of the first term in the expression for the activity coefficient.

Since different writers have used widely varying values for the dielectric constant of acetic acid, it was decided to measure it. This was done through the generous coöperation of Dr. J. Wyman of Harvard University. The values reported by Dr. Wyman for the glacial acetic acid employed in these experiments are: $\lambda = 8.586$ meters, $\epsilon = 6.274$; $\lambda = 8.590$ meters, $\epsilon = 6.279$; $\lambda = 3.792$ meters, $\epsilon = 6.236$; $\lambda = 3.791$ meters, $\epsilon = 6.234$. The mean of these values, 6.25, was used in calculation of the constants. This is in reasonably good agreement with the recent value of 6.16 obtained by Smyth.[17]

The activity coefficient of the salt saturating the solution is related to the measured solubilities by the equation

$$-\log f = -\tfrac{1}{2} \log P_{i_0}/P_i - \log f_0$$

where $P_i$ is the product of the ion concentrations of the saturating salt in the mixtures and $P_{i_0}$ is the same product for the salt in the absence of added salt. Since $f_0$, the activity coefficient of the salt in the pure solvent, is a constant, variations of the value of $-\tfrac{1}{2} \log P_{i_0}/P_i$ with concentration are equal to the variations of $-\log f$, and $-\log f_0$ may be calculated by extrapolation to zero concentration.

In order to see whether either Equation 1 or Equation 2 is applicable to the observed solubility changes, values of $-\tfrac{1}{2} \log P_{i_0}/P_i$ for the potassium perchlorate solutions have been plotted in Fig. 1 against the square roots of the total salt concentrations.

It may be noted that there is little difference between the curves obtained with three different added salts, two without and one with an ion common to the saturating salt. The curves closely approach the limiting slope of Equation 1 at the lower concentrations. This was not anticipated since comparable results in solvents of higher dielectric constant show consistent

[16] Hutchison and Chandlee, THIS JOURNAL, **53**, 2887 (1931).

[17] Smyth, *ibid.*, **52**, 1825 (1930). For the method used by Dr. Wyman see *ibid.*, **53**, 3292 (1931).

positive deviations. A fair agreement with the experimental data may be obtained with Equation 1 if a value of $a$ of $9 \times 10^{-8}$ is assumed. The curvature of the theoretical curve, however, is markedly less than those of the experimental curves.

Since Equation 2 has been shown to account for the positive deviations from the limiting slope which have been observed in other solvents, it might be expected to prove less satisfactory than Equation 1 in the present

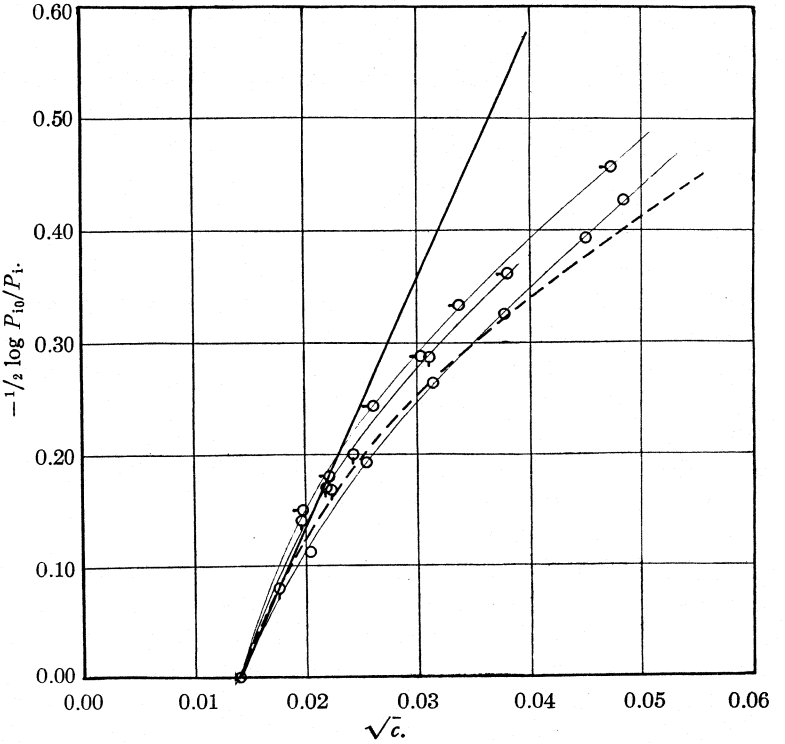


Fig. 1.—○, $KClO_4 + NaNO_3$; -○, $KClO_4 + NH_4NO_3$; ♀, $KClO_4 + NaBr$. ———, Limiting slope, Equation 1; – – –, Equation 2, $a = 9 \times 10^{-8}$.

case where in a solvent of much lower dielectric constant no such deviations are observed. This is not the case, however, for with $a = 9 \times 10^{-8}$ the curve obtained from Equation 2 gives a somewhat better agreement with the experimental curves. There is, however, a marked deviation at the higher concentrations. This curve is shown in the figure.

Although the curves predicted by Equations 1 and 2 are very nearly alike in the concentration range studied, a study of more dilute solutions where they differ more should show which is the more reliable. The experimental uncertainties make this very difficult. An empirical relationship which seems to hold quite generally for non-aqueous solutions may

throw some light on the question. This is that a very nearly linear relationship exists between the square root of the ion product and the square root of the total concentration. In Fig. 2 the solubilities of potassium perchlorate (equal to $\sqrt{P_i}$ in mixtures without a common ion) have been plotted against the square roots of the total salt concentrations in the sodium nitrate mixtures. The points are seen to lie on a straight line. Extrapolation of this line to zero concentration gives a value of $0.625 \times 10^{-4}$ for the hypothetical solubility of potassium perchlorate in a solution

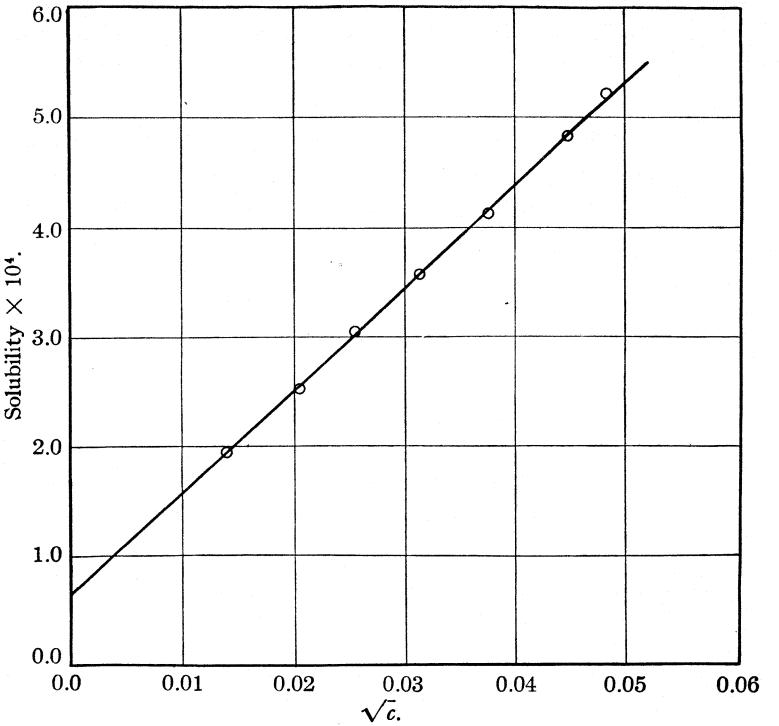


Fig. 2.—Solubility of potassium perchlorate in the presence of sodium nitrate.

of zero ionic strength. From this value the value of $-\log f_0$ can be calculated and is found to be 0.488. This is in much better agreement with the value of 0.450, obtained for $-\log f$ from Equation 2, using $a = 9 \times 10^{-8}$, than with the value 0.275 obtained from Equation 1 using $a = 9 \times 10^{-8}$. The maximum value, with $a$ equal to zero, obtainable from Equation 1 is 0.312. With $a = 8.5 \times 10^{-8}$ in Equation 2 an almost exact check would be obtained.

The changes of activity coefficients with concentration in more concentrated solutions may be calculated from the measurements of the solu-

bility of potassium nitrate. In Fig. 3 the values of $-1/2 \log P_{i_0}/P_i$ have been plotted against the square roots of the total salt concentration. It is seen that even at these concentrations, up to 0.045 mole per liter, the effect of adding different salts, one with and the other without a common ion, is the same within the limit of experimental uncertainties. Since Equations 1 and 2 differ less at higher concentrations, the theoretical curve for Equation 1 only is shown and with an $a$ value of $9.5 \times 10^{-8}$ agrees well with the results of our experiments without the introduction of a term involving change of dielectric constant.

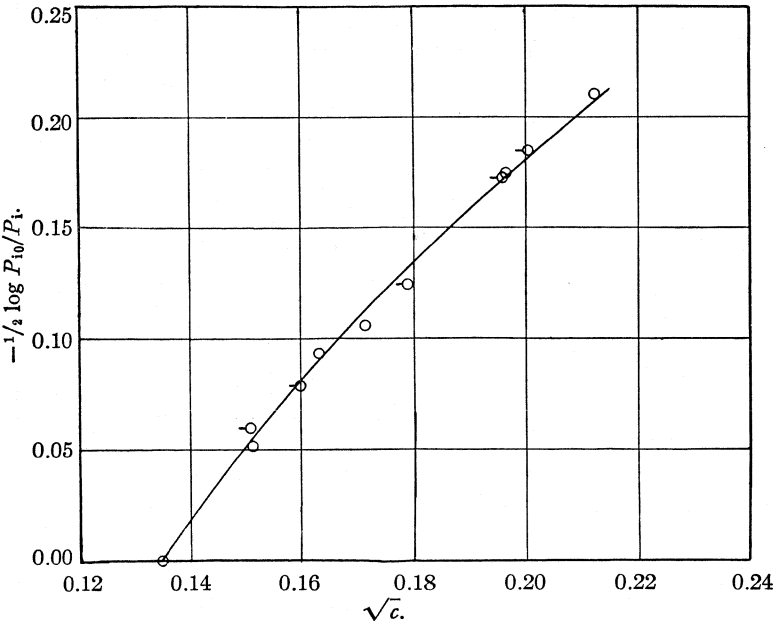


Fig. 3.—O, $KNO_3 + NH_4NO_3$; -O, $KNO_3 + NH_4Cl$. ——, Equation 1, $a = 9.5 \times 10^{-8}$.

The fact that the properties of solutions of the same salts in water and in other solvents may be explained by the interionic attraction theory when much smaller values for the ion diameters are employed indicates that the $a$ values assumed for the acetic acid solutions cannot be the true ion diameters independent of solvation. That this is not peculiar to acetic acid solutions is indicated by some preliminary solubility measurements made by the authors in ethyl acetate, with about the same dielectric constant, where the curves were found to have an even smaller slope than those for the acetic acid solutions. Apparently some property of the solvent in addition to the dielectric constant is necessary in order to explain the properties of solutions of salts in it.

## Summary

The solubilities of potassium perchlorate and potassium nitrate have been measured in the presence of several added salts in pure glacial acetic acid.

The observed solubilities agree with those predicted by the interionic attraction theory if a sufficiently large ion diameter is assumed.

An empirical relationship from which the value of the activity coefficient may be calculated has been pointed out.

A somewhat better agreement is obtained with the extended theory of Gronwall, La Mer and Sandved than with the original Debye–Hückel development.

It is concluded that explanation of the properties of salt solutions requires that other properties of the solvent in addition to its dielectric constant must be considered.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# THE VAPOR PRESSURES OF SATURATED AQUEOUS SOLUTIONS OF CERTAIN SALTS

BY H. W. FOOTE, BLAIR SAXTON AND J. K. DIXON

RECEIVED OCTOBER 7, 1931 PUBLISHED FEBRUARY 5, 1932

The literature of this subject has been summarized by Johnston and Leopold,[1] who pointed out, as have others, the difficulties of the usual static methods. One of the chief difficulties is in completely removing air from the saturated solution and another is in obtaining a solution for measurement which is neither supersaturated nor undersaturated. The above-mentioned writers found that equilibrium was established very slowly in their apparatus after removal of air by pumping, due presumably to difficulty in reaching complete saturation.

An apparatus which has been developed for another purpose has been found to avoid the difficulties mentioned above and to be suitable for determining the vapor pressure of saturated solutions from about 0° to somewhat above room temperature with an accuracy of approximately ±0.05 mm. The apparatus eliminates the error caused by air dissolved in the solution by forming the solution in the absence of air, and as the conditions are such that a saturated solution is formed very rapidly, equilibrium is established in a very short period of time.

## Apparatus, Procedure and Materials

A diagram of the apparatus, not drawn to scale, is shown in Fig. 1. In its essentials, it consists of a bulb A, for holding the salt and solution, connected to the bulb B con-

[1] Johnston and Leopold, THIS JOURNAL, 49, 1974 (1927).

taining air-free water, to a mercury manometer (diameter of the tube 6 mm.), and to a mercury vapor pump attached at C which was backed by an oil pump. The pressure could be reduced to approximately $10^{-4}$ mm. A McLeod gage, which however was not essential, was connected at D. The bulb for salt and saturated solution was connected by means of a ground-glass joint E containing a mercury seal, so that it could be disconnected and weighed as desired. The water in the bulb B had been boiled under diminished pressure at intervals over a period of several weeks before use, evaporating a considerable proportion of the water originally present and insuring the absence of dissolved air. The necessary stopcocks had been ground with great care and offered no difficulty from leakage.

For the determinations, the salt in weighed amount was introduced into its bulb and heated by means of a small electric oven for about eight hours at a temperature near 200° in the vacuum produced by the continuous action of the pumps. The bulb was then cooled and immersed in a two-liter Dewar flask containing water which was kept stirred and in which the temperature could be maintained very nearly constant during a determination. Below 10°, the variation in temperature was not more than ±0.04°, and above this temperature, the variation was about ±0.02°. The thermometer was checked against two standard thermometers.

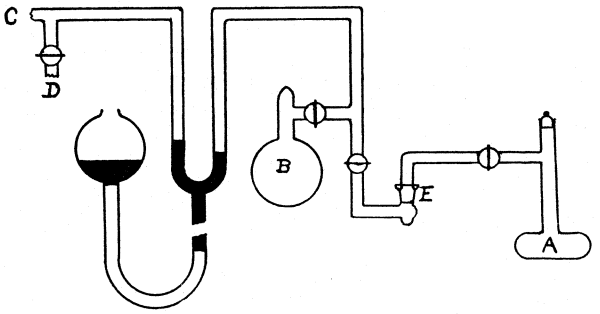


Fig. 1.

The saturated solution of the salt was produced by allowing vapor from the water bulb B to enter the salt bulb, where it condensed. By keeping the salt always in large excess, the liquid formed a saturated solution promptly. The pressure could then be determined by direct reading of the manometer, the readings being taken with a cathetometer. It is evident that air could be effectively eliminated by this method, but the question of whether a saturated solution could be formed promptly by the procedure required demonstration. There was also the possibility, if too little water was condensed on the finely divided crystals, that adsorption would take place, giving too low a value of vapor pressure. The fact that vapor pressures did not vary when the amount of vapor condensed varied rather widely, showed that the results were not influenced by adsorption. This does not mean that adsorption may not affect the vapor pressure if the liquid condensed is very small in amount, but it means that enough water was present to overcome this effect. To show that solutions were saturated, conditions were varied to promote undersaturation or the reverse by suitably varying the amount of condensed vapor and by temporary variation in temperature. It was found by these means that the pressures readjusted themselves to constant values rather rapidly. Ordinarily, equilibrium was established in about ten minutes, but readings were taken at ten-minute intervals for a period of an hour. In one case (that of potassium sulfate at 0°), it was demonstrated that the pressure obtained at the end of ten minutes was identical with

that obtained at the end of twenty-four hours. At least two series of determinations were made, one on rising and the other on falling temperature, varying also the amount of condensed vapor, without any effect being evident from the different conditions greater than the error in reading pressure. The weight of salt taken varied between 3.5 and 9 g. and of water, between 0.08 and 0.85 g.

Except for cesium chloride, all salts were purified by usual methods and it is quite certain that errors introduced by impurities are less than the error in reading the manometer. The sample of cesium chloride was obtained from Dr. O. E. Schupp of this Laboratory, who had purified it by special methods applicable to cesium salts.

The corrections applied to measured pressures to reduce to pressures in millimeters of mercury at 0° were taken from the "International Critical Tables."

## Vapor Pressures

The thermodynamic equation giving the change in equilibrium pressure with temperature for any univariant system has been given by Gibbs.[2] For the three phase system here considered, this becomes

$$\frac{dP}{dT} = \frac{S' + S''' - S''}{V' + V''' - V''} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \qquad (1)$$

where $S$ and $V$ represent the total entropy and total volume of a phase and the single accent refers to the vapor, the double to the liquid, and the triple to the crystalline phase. Using molal and partial molal values, this becomes

$$\frac{dP}{dT} = \frac{n_1 H_1' + n_2 H_2''' - n_1 \bar{H}_1'' - n_2 \bar{H}_2''}{T(n_1 V_1' + n_2 V_2''' - n_1 \bar{V}_1'' - n_2 \bar{V}_2'')} = \frac{n_1 \Delta H_v - n_2 \Delta H_s}{T(n_1 \Delta V_v - n_2 \Delta V_s)} \qquad (2)$$

where $\Delta H_v$ is the molal heat of vaporization of pure water, $\Delta H_s$ is the molal heat of solution of the salt to give a saturated solution, $\Delta V_v$ is the volume increase on vaporizing a mole of pure water, $\Delta V_s$ is the volume increase on the solution of one molal of salt to give a saturated solution, and $n_1$ and $n_2$ are the number of moles of water and salt, respectively, in the saturated solution.

Neglecting the volumes of the condensed phases, assuming the validity of the ideal gas law for water vapor, expressing the composition of the solution on the molality basis, and the heats in calories, we have

$$253.96 \frac{d \log P}{d(1/T)} = -(55.51 \Delta H_v - m_2 \Delta H_s) = -\Delta H' \qquad (3)$$

which is one form of the equation of van't Hoff.[3]

Equation 3 can be evaluated, thus getting the slope of the $\log P - (1/T)$ curve, or it can be integrated and $\log P$ expressed as a function of $T$, if $\Delta H'$ is a known function of $T$. It is obvious that

$$\frac{d \Delta H'}{dT} = 55.51\, c_{p_1}' + m_2 c_{p_2}''' - C + \left(H_2''' - \frac{\partial H}{\partial m_2}\right) \frac{\partial m_2}{\partial T} \qquad (4)$$

[2] Gibbs, Equation (129), "On the Equilibrium of Heterogeneous Substances," *Trans. Connecticut Acad.*, **3**, 108 (1876); "The Collected Works of J. Willard Gibbs," Longmans, Green and Co., New York, 1928, Vol. I, p. 55.

[3] Van't Hoff, "Vorlesungen über theoretische und physikalische Chemie," Friedrich Vieweg und Sohn, Braunschweig, 1898, Vol. I, p. 33.

where $C$ is the total heat capacity, $H$ the total heat content of a quantity of saturated solution containing 1000 grams of water and $c'_{p_1}$ and $c'''_{p_2}$ are the molal heat capacities of water vapor and crystalline salt, respectively. Then

$$\Delta H'_{(T)} = \Delta H'_{(T_0)} + \int_{T_0}^{T} \Delta C_p \, d\,T + \int_{T_0}^{T} \left( L_2''' - \frac{\partial L}{\partial m_2} \right) \frac{\partial m_2}{\partial T} \, d\,T \qquad (5)$$

where $\Delta C_p = 55.51\, c'_{p_1} + m_2 c'''_{p_2} - C$; $L_2'''$ is the relative molal heat content of the crystalline salt; and $L = m_2 (\Delta H_s + L_2''')$ is the relative heat content of a saturated solution containing 1000 g. of water. Hence

$$253.96 \frac{d \log P}{d\,(1/T)} = -\Delta H'_{(T_0)} - \int_{T_0}^{T} \left[ \Delta C_p + \left( L_2''' - \frac{\partial L}{\partial m_2} \right) \frac{\partial m_2}{\partial T} \right] d\,T \qquad (6)$$

and

$$253.96 \log P = -\frac{\Delta H'_{(T_0)}}{T} - \frac{1}{T} \int_{T_0}^{T} \left[ \Delta C_p + \left( L_2''' - \frac{\partial L}{\partial m_2} \right) \frac{\partial m_2}{\partial T} \right] d\,T + \int \frac{\Delta C_p + \left( L_2''' - \frac{\partial L}{\partial m_2} \right) \frac{\partial m_2}{\partial T}}{T} \, d\,T + i \qquad (7)$$

Of the systems studied in this paper, there are sufficiently accurate thermal data in the literature in only two cases, sodium and potassium chlorides, to justify the use of equations (6) and (7). These data are given in Table I.

TABLE I

| Substance | $T_0$ | $\Delta H_{v(T_0)}$ | $m_2$ | $\Delta H_{s(T_0)}$ |
|---|---|---|---|---|
| NaCl | 298.1 | 10,484[a] | 6.145[b] | 466[d] |
| KCl | 298.1 | 10,484[a] | $-7.71 + 0.042\ T$[b] | 3692[d] |
| | $c'_{p1}$ | $c'''_{p2}$ | $C$ | $\Delta C_p$ |
| NaCl | 8.44[e] | 12.15[g] | 1063[f] | −520 |
| KCl | 8.44[e] | 12.38[g] | 968[c] | $-595 + 0.52\ T$ |
| | $L_2'''$ | $L$ | | |
| NaCl | | | | |
| KCl | −4285 | $1534 - 910\ m_2$ | | |

[a] "International Critical Tables," Vol. V, p. 138. [b] *Ibid.*, Vol. IV, pp. 235, 239. [c] *Ibid.*, Vol. V, p. 115. [d] Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925). [e] Lewis and Randall, "Thermodynamics," p. 80. [f] *Ibid.*, p. 85. [g] Russell, *Physik. Z.*, **13**, 59 (1912).

From these data and the measured vapor pressures, the following equations were derived

$$\text{(NaCl)} \quad \log P = -\frac{2890.7}{T} - 4.715 \log T + 22.612 \qquad (8)$$

$$\text{(KCl)} \quad \log P = -\frac{2995.5}{T} - 6.680 \log T + 0.001024\ T + 27.569 \qquad (9)$$

In the remaining cases, $\Delta H'$ was assumed to be constant in the temperature interval used and the best empirical constants were determined for an equation of the type

$$\log P = -\frac{A}{T} + B \qquad (10)$$

Thus the vapor pressures of the other three saturated solutions are given by the equations

$$(CsCl) \quad \log P = -\frac{2198.5}{T} + 8.5621 \tag{11}$$

$$(K_2SO_4) \quad \log P = -\frac{2332.5}{T} + 9.1881 \tag{12}$$

$$(Na_2SO_4) \quad \log P = -\frac{2696.6}{T} + 10.3630 \tag{13}$$

The differences between the vapor pressures calculated by Equations 8–13 and those measured are shown in the diagram, Fig. 2. The average

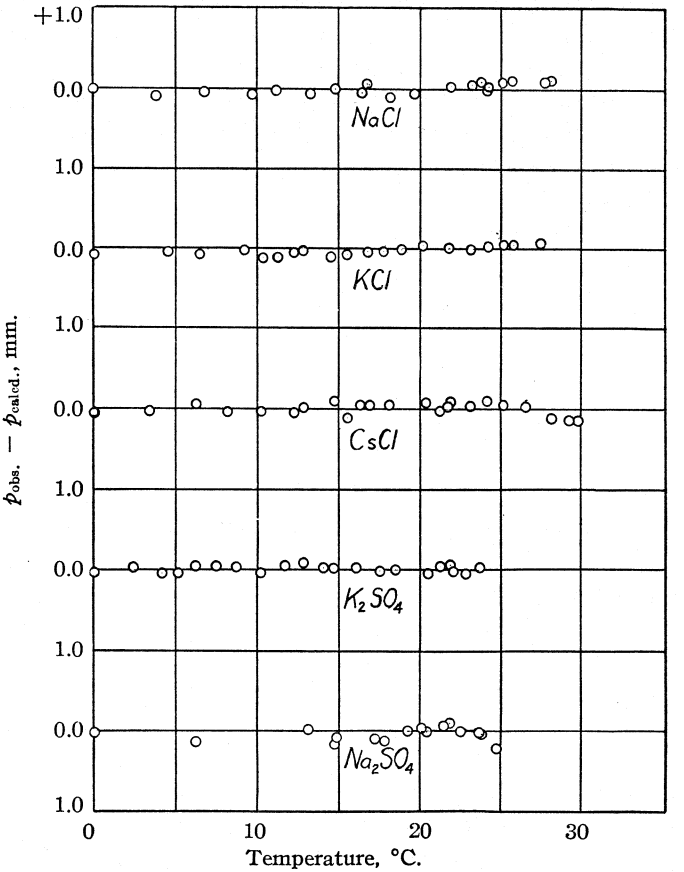


Fig. 2.—$p_{obs.} - p_{calcd.}$ as a function of temperature.

deviation between observed and calculated results is ±0.05, which is approximately the error of observation in reading pressures. It is probable that the values for sodium sulfate are the least accurate, as they were the first determined.

It is clear from Equation 3 that the heat of solution of a salt in forming a saturated solution can be calculated from the temperature coefficient of the vapor pressure of the saturated solution if this is of sufficient accuracy, but that, in general, the measurements must be carried out with greater precision than those in this investigation, which were not done with this end in view. However, we have made the attempt for the two cases (sodium and potassium chlorides) for which there are measured data.

From the slope of the log $P$–$(1/T)$ curve for potassium chloride, we obtained 3490 at 25°, which differs from the measured value by 5.4%. The result with sodium chloride was unsatisfactory. Finally, the $A$ constant for sodium sulfate shows that the heat of solution is negative.

The system with sodium sulfate which we investigated is metastable below 32° and should have yielded a mixture of the anhydrous salt and decahydrate instead of the saturated solution of the anhydrous salt, but the metastable system always formed in preference to the other. After some difficulty, the transformation to the stable system was accomplished and the following vapor pressures were determined in the order given, first adding and then removing water.

SYSTEM $Na_2SO_4 \cdot 10H_2O$–$Na_2SO_4$–VAPOR

$T$, 24.75° $Na_2SO_4$, 5.7575 g.

| | | | | | | |
|---|---|---|---|---|---|---|
| $P$..... | 18.90 | 18.85 | 18.85 | 18.85 | 18.80 | 18.80 |
| Wt. $H_2O$, g. | 0.2459 | 0.3217 | 0.4149 | 1.2320 | 1.1765 | 1.0984 |

The results of Baxter and Lansing[4] give a value of 19.00 mm. when their interpolation formula is used.

## Summary

A modified static apparatus has been described for measuring the vapor pressures of saturated salt solutions. The vapor pressures of saturated solutions of sodium chloride, potassium chloride, cesium chloride, potassium sulfate and sodium sulfate—the last, a metastable system—have been measured from 0° over a range of temperature approximating 25°.

The temperature coefficients of the vapor pressures of saturated solutions of potassium chloride and sodium chloride have been calculated from thermal data, thus allowing a comparison between observed and calculated vapor pressures. The differences, shown in Fig. 2, average ±0.05 mm.; which is approximately equal to the error of observation.

In the three other systems thermal data are lacking and vapor pressures have been calculated by the expression $\log P = -(A/T) + B$. The differences between observed and calculated values, also shown in Fig. 2, average ±0.06 mm.

NEW HAVEN, CONNECTICUT

[4] Baxter and Lansing, THIS JOURNAL, **42**, 149 (1920).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# THE QUENCHING OF MERCURY RESONANCE RADIATION. II. FURTHER HYDROCARBONS AND NITRIC OXIDE[1]

BY JOHN R. BATES

RECEIVED OCTOBER 10, 1931 PUBLISHED FEBRUARY 5, 1932

The effectiveness of the hydrocarbons of the series methane, ethane, propane and butane in quenching the resonance radiation of mercury was given in Part I. The work here presented[2] extends these measurements to hydrocarbons containing a larger number of carbon atoms representing the saturated, unsaturated and benzene hydrocarbons. Nitric oxide is included as one of the few diatomic gases which have not been measured by the improved method used,[3] although Noyes[4] has published an estimated effective cross section obtained in his investigation of the decomposition of this gas under the influence of excited mercury atoms. It was hoped that an extension to as large a number of molecules as possible would aid in a clarification of the theories connected with the structure of molecules and their ability to take over the energy of excitation of mercury atoms in the $2^3P_1$ state.

## Experimental

The methods of measurement are given in Part I of this work. In measuring low pressures of the high-boiling hydrocarbons it became necessary to use the gage described by Foote and Dixon[5] for the measurement of liquids of low vapor pressures. An additional refinement, which removed the necessity of constantly checking the temperature of the liquid mercury supplying mercury vapor to the resonance lamp and quenching vessel, was added. Water from a thermostat constant to within 0.1° was pumped through the Dewar flasks in which these mercury reservoirs were placed.

In working with the non-volatile hydrocarbons it was found that no stopcocks could be used in the system, since the vapors of these substances dissolved in the stopcock grease and then, upon pumping, evaporated slowly, or even evaporated from the grease on the other outlet of the stopcock, making the regulation and measurement of pressures impossible. All stopcocks were, therefore, replaced by mercury cut-offs.

The pure hydrocarbons were dried over phosphorus pentoxide and subjected to fractional distillation *in vacuo*. The nitric oxide was prepared by the action of a solution of sodium nitrite in concentrated sulfuric acid upon liquid mercury. The gas was then dried with phosphorus pentoxide,

[1] Presented at the Fall Meeting of the American Chemical Society, Buffalo, 1931.

[2] Bates, THIS JOURNAL, **52**, 3825 (1930).

[3] Zemansky, *Phys. Rev.*, **36**, 919 (1930).

[4] Noyes, THIS JOURNAL, **53**, 514 (1931).

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

and subjected to a vacuum distillation. It was stored in a bulb containing mercury droplets, which remained untarnished after several months, showing the absence of oxygen in the gas. Had oxygen been present the nitrogen peroxide resulting from its reaction with nitric oxide would have rapidly tarnished the mercury surfaces.

## Experimental Results

The values of $J$, the percentage of resonance radiation emitted, are given below for various pressures of the gases. The pressures are expressed in millimeters of mercury.

TABLE I

EXPERIMENTAL VALUES

| *n*-Heptane | | 2,2,3-Trimethylbutane | | Benzene | |
|---|---|---|---|---|---|
| $P$, mm. | $J$ | $P$, mm. | $J$ | $P$, mm. | $J$ |
| 0.0220 | 90.0 | 0.0487 | 85.8 | 0.008 | 92.3 |
| .0308 | 86.5 | .096 | 71.9 | .013 | 87.6 |
| .0432 | 82.6 | .136 | 64.6 | .024 | 82.2 |
| .0489 | 81.9 | .154 | 60.2 | .039 | 75.5 |
| .0510 | 82.0 | | | .078 | 64.1 |
| .0690 | 74.9 | | | | |
| .0899 | 69.0 | | | | |
| .0930 | 69.0 | | | | |
| .119 | 62.8 | | | | |
| .124 | 61.0 | | | | |
| Nitric oxide | | 1 Heptene | | 3 Heptene | |
| 0.0207 | 87.1 | 0.0123 | 90.4 | 0.0162 | 83.3 |
| .0264 | 83.4 | .022 | 84.9 | .0287 | 75.3 |
| .0331 | 76.9 | .022 | 81.9 | .0527 | 65.3 |
| .0507 | 71.5 | .022 | 81.4 | .084 | 55.9 |
| .108 | 50.7 | .029 | 76.4 | .171 | 38.5 |
| | | .053 | 67.9 | | |

From these values of $P$ and $J$ may be obtained the value of $GK/P$, where $K$ is the number of effective collisions per second and $G = 10^{-7}$ the mean life of the excited mercury atom, and $\Sigma_E^2$, the effective cross section of the collision process, $\Sigma_E$ being the sum of the effective radii in collision. The method of calculation appears in the earlier work. These values are tabulated in Table II.

TABLE II

CALCULATED VALUES

| | $GK$ | $\Sigma_E^2 \times 10^{16}$ | | $GK$ | $\Sigma_E^2 \times 10^{16}$ |
|---|---|---|---|---|---|
| Nitric oxide | 1.25 | 24.7 | 3-Heptene | 1.78 | 55.9 |
| *n*-Heptane | 0.760 | 24.0 | 1-Heptene | 1.46 | 45.8 |
| 2,2,3-Trimethylbutane | 0.625 | 19.7 | Benzene | 1.42 | 41.9 |

## Discussion of Results

The values of the effective cross sections of these molecules are without exception the largest that have been found, with the use of the method here

employed, which, according to the theoretical calculations of Zemansky,[6] gives a more accurate value than those previously in use. However, for the larger molecules it is not surprising that this should be the case.

In considering the relation of effective cross section to the structure of the molecule, there are several factors which must be taken into account. These may be divided, in a purely formal manner, into three classes, electronic, energetic and spatial.

The principle of conservation of spin angular momentum of the electronic system of two atoms in collision was proposed by Wigner,[7] and Beutler and Eisenschimmel[8] have tested it experimentally and found that in energy transfers where it is obeyed there is a much greater probability than in those cases where there is a change in total spin angular momentum in the energy interchange. Thus collisions in which a krypton atom in a triplet ($2^3P_2$) state gives its energy of activation to a mercury atom ($1^1S_0$) raising it to a singlet state ($5^1D_2$) are much less probable than those which result in a mercury atom in a triplet ($5^3D_n$) state, since the krypton atom falls to a singlet state ($1^1S_0$) and the total spin or multiplicity remains the same in the latter case. Thus in the two equations

$$Kr(^3P_2) + Hg(^1S_0) \longrightarrow Kr(^1S_0) + Hg(^1D_2) \quad (1)$$
$$Kr(^3P_2) + Hg(^1S_0) \longrightarrow Kr(^1S_0) + Hg(^3D_n) \quad (2)$$

the total spin on the left-hand side is equal to 1 in both cases, while on the right (1) gives a spin of 0 and (2) a spin of 1, the same as the original two molecules.

It must be pointed out that the principle is identical with the spectroscopic selection rule which states that only terms of like multiplicity can intercombine, which in helium is obeyed, but in large atoms such as mercury breaks down, since, for example, the strong 2536 line of mercury is a $^3P_1 \longrightarrow {}^1S_0$ transition. It does not, therefore, hold that the "forbidden" transfers of energy will be completely absent, but that they will be considerably less frequent. It might also be mentioned that the rule will hold for the steps in chain reactions.

Of the molecules which have been measured all are in a singlet state with the exception of oxygen, which has a $^3\Sigma$ normal state and nitric oxide which has a $^2\Pi$.

Hydrogen has already been treated by Beutler and Eisenschimmel who showed that either of the two dissociation processes

$$H_2(^1\Sigma) + Hg(^3P) \longrightarrow H(^2S) + H(^2S) + Hg(^1S)$$
$$H_2(^1\Sigma) + Hg(^3P) \longrightarrow H(^2S) + HgH(^2\Pi) + Hg(^1S)$$

is in accord with the conservation of spin, and also energetically possible.

[6] Zemansky, *Phys. Rev.*, **36**, 919 (1930).

[7] Wigner, *Nachr. Götting. Ges.*, 375 (1927).

[8] Beutler and Eisenschimmel, *Z. physik. Chem.*, **10**, 89 (1930).

Leaving out of consideration for the present these three cases, we find that the effective cross sections of the remaining molecules are considerably less than the normal cross sections as determined from gas kinetic data. Furthermore, there exists evidence that the molecules $N_2$, CO, $NH_3$, $CH_4$ and $H_2O$ quench the $^3P_1$ mercury atom to the $^3P_0$ metastable level, while there is no indication one way or the other for $CO_2$, $C_2H_6$, $C_3H_8$, $C_4H_{10}$, although Zemansky assumes these to do the same thing. If the mercury atom should lose its energy to return to the $^1S$ normal state and the molecule receiving the energy remains in its normal $^1\Sigma$ state, but in a higher vibrational state, the spin angular momentum would not be conserved. However, in the drop of the mercury from $^3P_1$ to $^3P_0$ with the quenching molecule remaining a $^1\Sigma$ the total spin remains unchanged, and we see this to be the preferred process, at least for the cases mentioned. It should perhaps be emphasized that the evidence for this transition, which consists in observing absorption of mercury of lines which originate in the $^3P_0$ state[9] and also the apparent decrease in quenching at high pressures or temperatures,[10,2] does not at all preclude the possibility that some fraction of the mercury atoms are being quenched to the normal state. It does, however, show that the transition $^3P_1 \longrightarrow {}^3P_0$ is very prevalent, which it should be if the conservation of spin represents a large factor in the probability of transition.

In the case of $O_2$ and NO we find cross sections larger than those obtained from gas kinetic data. There are two possible ways in which the oxygen molecule can take up the 4.86 volts of energy which are given up in the $^3P_1 \longrightarrow {}^1S_0$ transition

$$Hg(^3P_1) + O_2(^3\Sigma) \longrightarrow Hg^1S_0 + O_2(^3\Sigma) + \text{vib. energy} \quad (1)$$
$$Hg(^3P_1) + O_2(^3\Sigma) \longrightarrow Hg(^1S_0) + O_2(^1\Sigma) + \text{vib. energy} \quad (2)$$

It is obvious that both (1) and (2) have the spin conserved. Wigner (private communication) considers that (2) would, on the basis of spin, be more probable by a factor of three than would (1).

With NO either of these two processes answers the spin requirements

$$Hg(^3P_1) + NO(^2\Pi) \longrightarrow Hg(^1S_0) + NO(^2\pi) + \text{vib. energy} \quad (1)$$
$$\longrightarrow Hg(^3P_0) + NO(^2\Pi) + \text{vib. energy} \quad (2)$$

From the consideration of the ability of the molecules to receive the energy of the mercury atom it has been shown theoretically by Kallman and London[11] and Rice[12] that the closer the energy level of the receiving atom or molecule to the energy to be received, the more probable the transition. Beutler and Josephy[13] have studied the transition between

[9] R. W. Wood, *Proc. Roy. Soc.* (London), **106**, 679 (1924); *Phil. Mag.*, **50**, 774 (1925); Wood and Gaviola, *ibid.*, **5**, 271 (1928).

[10] Cario and Franck, *Z. Physik*, **17**, 202 (1923).

[11] Kallman and London, *Z. physik. Chem.*, [B] **2**, 207 (1929).

[12] Rice, *Proc. Nat. Acad. Sci.*, **17**, 34 (1931).

[13] Beutler and Josephy, *Z. Physik*, **53**, 747 (1929).

excited mercury atoms and sodium atoms and indicated that this can be shown experimentally. Zemansky has classed the cross sections obtained for transitions from $^3P_1$ to $^3P_1$, which represents an energy of 0.218 volt and again shown that the closer an energy state of the molecule is to this value the larger the cross section. However, in choosing between the two possible jumps $^3P_1 \longrightarrow {}^3P_0$ and $^3P_1 \longrightarrow {}^1S_0$ it is not possible to use the energy resonance as a criterion. For example, $N_2$ and CO have vibration levels which lie at 4.86 and 4.82 volts, as determined by extrapolating the expressions for their vibrational frequencies given in the "International Critical Tables." These are in much closer agreement to 4.86 volts than are the first vibrational levels to 0.218 volt, which is the energy difference between the $^3P_1$ and $^3P_0$ states.

Thus the energy relationships hold true only in the cases of a single type of electronic transition which, as has been shown, may quite conceivably be governed by the necessity of having the total spin conserved. In the cases of $O_2$ and NO where this latter selection rule is obeyed and it seems possible to have the whole 4.86 volts transferred, there are also vibrational energy levels in these molecules fairly close to this value; namely, 4.86 for $O_2{}^3\Sigma$, 4.90 for $O_2{}^1\Sigma$ and 4.90 for $NO^2\Pi$.[14] Zemansky suggests that the mercury atom reacts with the oxygen molecule $Hg' + O_2 \longrightarrow HgO + O$ but as Noyes points out an error crept into his calculations and the close energy agreement to which he ascribes the large cross section for oxygen is non-existent. The process is also doubtful because of chemical evidence which shows that more oxygen molecules are activated than there are mercury atoms present in the system.

For diatomic molecules there is no necessity for a consideration of the space occupied by the two atoms since this is introduced in the eigenfunctions whereby the probabilities are calculated. Moreover, the differences in the cross section due to this would be negligible in comparison with the other factors. However, as we go up an homologous series of compounds such as the saturated hydrocarbons it is obvious that the effective cross section must depend to a progressively larger extent on the space configuration of the atoms of the molecule. Not only is it a matter of placing the carbon atoms in an alternating chain which is demanded by the tetrahedral nature of the valence forces of the carbon atom, but also, due to the fact that there exists free rotation around a single carbon–carbon bond, there are more and more possible arrangements for the configuration as the number of carbon atoms increases above three. This effect increases the effective area offered to a colliding atom by such molecules. Zemansky, in incorporating into his results the values for the cross section of the hydrocarbons, does not take this into consideration, though it would probably be of some importance in the case of butane. The value of the

[14] A. C. G. Mitchell, *J. Franklin Inst.*, **206**, 817 (1928).

cross section for heptane, furthermore, does not fit into Zemansky's curve for the variation of this magnitude with the difference in energy between the nearest infra-red band of the molecule and the 0.218 volt which the mercury atom gives up. The band in heptane, according to the data of Coblentz,[15] from which the data of Zemansky were also derived, should be at 5.81, which is equivalent to 0.212 volt.[16] This value should, according to his curve, give a cross section smaller than butane, while actually it is almost five times as large. This is almost certainly due to these spatial considerations. In discussing these hydrocarbons, it must also be borne in mind that there exists no evidence that the quenching is to the metastable level, except in the case of methane. In fact the work of Taylor and Hill,[17] who showed that the hydrocarbons, with the exception of methane, are decomposed by excited mercury atoms, lends considerable doubt to the supposition that these molecules quench by the deactivation process $2^3P_1 \longrightarrow 2^3P_0$. While the decomposition might occur by a double deactivation process $2^3P_1 \longrightarrow 2^3P_0 \longrightarrow 1^1S_0$, the second step furnishing the energy necessary to break up the molecule, there are no grounds upon which to base the assumption of such a complicated mechanism. For these reasons it would seem that the hydrocarbons, with the exception of methane, should not be taken into account in considering the variation of effective cross section with the resonance between the energy states of molecules and the energy difference between the $2^3P_0$ and $2^3P_1$ levels of mercury.

The value of $\Sigma_E^2$ for nitric oxide of $24.7 \times 10^{-16}$ sq. cm. is the largest cross section found among the diatomic molecules. The value obtained by the method employed here is very much larger than the value of $2.10 \times 10^{-16}$ reported by Noyes in his measurements. However, Noyes in a private communication has informed the author that a recalculation of his results has raised his cross section to a value not incompatible with the result here presented, when the differences in experimental method are considered. As has been discussed in an earlier section, the principle of conservation of spin angular momentum is obeyed for both processes of deactivation of mercury by nitric oxide. Noyes has discussed at length the various possible mechanisms whereby the nitric oxide might act with mercury. He has come to the conclusion that his work gives some evidence that the process involves the $2^3P_1 \longrightarrow 2^3P_0$ transition of the mercury atom. If, now, we plot the values of $\Sigma_E^2$ against the energy values of the vibrational frequencies expressed in volts of the molecules involved, we obtain the results shown in Fig. 1. The point 0.218 volt represents the

[15] Coblentz, "Investigations of Infra-Red Spectra," Carnegie Institute of Washington, 1905.

[16] *n*-Heptane is not measured by Coblentz, but both *n*-hexane and *n*-octane have this band at this wave length, from which there is apparently no large deviation even up to hydrocarbons of very long chain length ($C_{24}H_{50}$).

[17] Taylor and Hill, THIS JOURNAL, **51**, 2922 (1929).

energy of $2^3P_1 \longrightarrow 2^3P_0$ transition of the mercury atom. The line at 0.244 represents the addition to this of the average kinetic energy, *kt*, possessed by the colliding atoms and molecules. The curve thus obtained is symmetrical to either of these two points The values of the hydrocarbons are omitted and the value for carbon dioxide should perhaps not be used in this connection since it is not at all established that this molecule brings about the transition here under consideration. It is merely plotted to show how far off any resonance curve it falls. Zemansky, due to his inclusion of the hydrocarbons, was led to believe that it was carbon monoxide which did not agree with the other values. The latter molecule is however known to produce transitions to the metastable level, and fits the curve very well if the hydrocarbons are not included and the value for nitric oxide is taken into consideration. It is not to be expected that these points will lie on a smooth curve, as there are variables other than the energy resonance which must be taken into consideration. For example, the masses of the molecules will alter the probability of energy transfers in collisions of the second kind.[18] This type of curve is, however, in agreement with the results derived theoretically, even to the asymmetry of the resonance curve.[19]

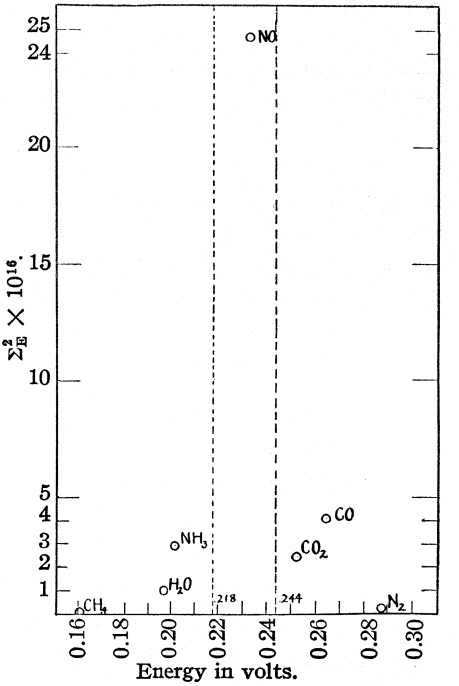


Fig. 1.

The large cross section for the two heptenes is undoubtedly connected with the presence of the double bond. As to the existence of such a large difference in the cross sections of the two isomers, this may be due to the effect on spatial arrangement of the molecule of the fact that there is no rotation around a double bond.

[18] Morse and Stueckelberg, *Ann. Physik*, [5] **9**, 579 (1931).

[19] The statement of Morse and Stueckelberg that the asymmetry of the resonance curve found by them theoretically is borne out by Zemansky's experimental values is incorrect. The position of the asymmetry found by the latter is directly opposite to that predicted. This, however, is not surprising, since the cross section will be affected by factors other than the energy difference, which is not allowed for in either curve. In fact, it is a mistake to draw a curve through the experimental curves without correcting for the other factors involved.

The size of $\Sigma_E^2$ for benzene, which is greater than the gas kinetic value of 21.9, is of interest principally because in the work of Bates and Taylor[20] this substance, when subjected to the action of excited mercury atoms, gave very little permanent gas. As was observed in that work the action of the mercury probably results for the most part in the removal of a hydrogen atom, which then recombines with other benzene molecules to form hydrobenzenes.

The author is indebted to the Research Laboratories of the General Motors Corporation for the pure hydrocarbons used in these measurements.

## Summary

The quenching of mercury resonance radiation by nitric oxide, benzene, *n*-heptane, 2,2,3-trimethylbutane, 2-heptene and 3-heptene has been measured, and values of the effective cross sections of these molecules have been calculated. A general arrangement of molecules which correlates their effective cross sections and structure has been discussed.

[20] Bates and Taylor, THIS JOURNAL, **49**, 2483 (1927).

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# SOLUBILITY OF THALLOUS CHLORIDE IN SOLUTIONS OF GLYCINE AND GLYCINE SALTS[1]

BY CRAWFORD F. FAILEY

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The solubilities of salts in the presence of amino acids have been little investigated. Bjerrum[2] reported the solubility of dinitrotetrammine-cobaltinitrate $[Co(NH_3)_4(NO_2)_2]NO_3$ as about 8% greater in $N/10$ glycine than in water. Knowledge concerning the activity coefficients of strong electrolytes in the presence of amino acids would be valuable, however, in the determination of dissociation constants for amino acids themselves, it being necessary to calculate from the measured hydrogen-ion activity what concentration of free hydrogen or hydroxyl ion is present. Some assumption as to activity coefficients is therefore required. For example Birch and Harris[3] assumed $\gamma_{H^+}$ and $\gamma_{OH^-}$ to have the same value as in an ampholyte-free solution of identical salt concentration.

## Experimental

The thallous chloride used in this investigation was a C. P. preparation recrystallized from distilled and from conductivity water. Theoretical nitrogen values were found for

[1] This work was aided by grants from the Chemical Foundation.

[2] Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).

[3] Birch and Harris, *Biochem. J.*, **24**, 564 (1930).

the recrystallized glycine. The nitric acid was distilled from silver nitrate, and sodium hydroxide from sodium was free from chloride and carbonate.

Approximately 10 g. of thallous chloride was shaken with the solvent to be used; the latter was then replaced by a fresh portion of about 200 ml. and the mixture rotated overnight in a water thermostat at a temperature of 25.00 ± 0.01°. In weighed samples chlorides were determined gravimetrically as silver chloride, it having been shown that glycine did not interfere. Each solubility recorded in Tables I and II is the average of at least two equilibrations, the duplicates usually agreeing within 0.1%. In order to check the composition of the solid phase a sample was also removed from each of the most concentrated solvents and shown by analysis to consist of thallous chloride.

## Discussion

Six determinations gave the solubility in water as 0.01617 ± 0.00002 mol per 1000 g. of water. In Table I are shown the results for solvents

TABLE I

RESULTS FOR SOLVENTS WITH GLYCINE

| Glycine molality | Soly. × $10^5$ | $-\log \gamma_{\pm}$ | $\gamma_{\pm}$ |
|---|---|---|---|
| 0.000 | 1617 | 0.072 | 0.847 |
| .010 | 1623 | .073 | .845 |
| .030 | 1634 | .076 | .840 |
| .050 | 1648 | .080 | .832 |
| .100 | 1678 | .088 | .817 |
| .200 | 1745 | .105 | .785 |

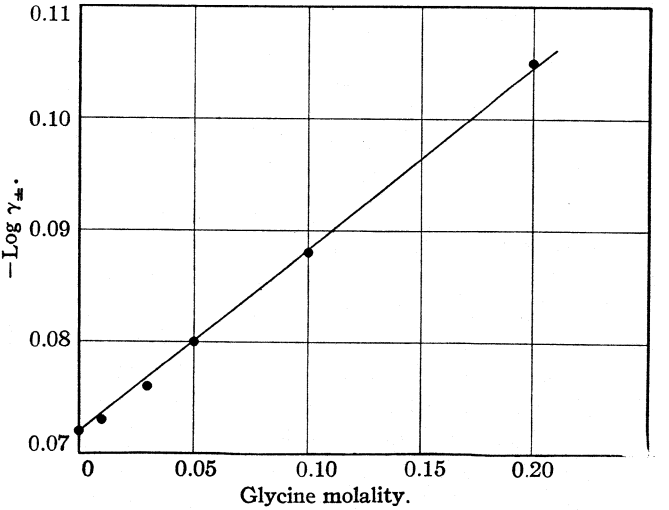


Fig. 1.

containing only glycine. The first column indicates the solvent, the second thallous chloride solubility, the third values of $-\log \gamma_{\pm}$ calculated by means of the equation $-\log \gamma_{\pm} = \log 1/m_{\pm}^{\circ} \log 1/m_{\pm}$ on the assumption that log

$1/m_{\pm}^{\circ} = 1.8630$.[4] In the fourth column are the activity coefficients. The compositions of the solutions are expressed as mols per 1000 g. of water *in vacuo*.

Figure 1, which is a plot of the above data with $-\log \gamma_{\pm}$ as ordinate and glycine molality as abscissa, shows that $-\log \gamma_{\pm}$ for thallous chloride is approximately a linear function of the glycine molality.

Solubilities in solutions of nitric acid and of sodium hydroxide are recorded in the first eight rows of Table II. The last eight rows represent the same solvents except that one-tenth mole of glycine has been added per 1000 g. of water. The first, second, third and fourth columns are as in Table I. Column five is the square root of the ionic strength, the latter being taken as the sum of thallous chloride plus acid or base.

TABLE II

SOLUBILITIES IN OTHER SOLVENTS

| Solvent | Soly. × $10^3$ | $-\log \gamma_{\pm}$ | $\gamma_{\pm}$ | $\sqrt{\mu}$ |
|---|---|---|---|---|
| $HNO_3$ $M$ = 0.025 | 1734 | 0.102 | 0.791 | 0.206 |
| .050 | 1821 | .123 | .753 | .261 |
| .075 | 1887 | .139 | .726 | .307 |
| .100 | 1945 | .152 | .705 | .346 |
| NaOH $M$ = 0.025 | 1777 | .113 | .771 | .207 |
| .050 | 1896 | .141 | .723 | .263 |
| .075 | 1995 | .163 | .687 | .308 |
| .100 | 2086 | .182 | .658 | .346 |
| Glycine $M/10$ + $HNO_3$ $M$ = 0.025 | 1794 | .117 | .764 | .207 |
| .050 | 1868 | .134 | .735 | .262 |
| .075 | 1925 | .147 | .713 | .307 |
| .100 | 1979 | .159 | .693 | .346 |
| Glycine $M/10$ + NaOH $M$ = 0.025 | 1810 | .121 | .757 | .208 |
| .050 | 1902 | .142 | .721 | .263 |
| .075 | 1978 | .159 | .693 | .308 |
| .100 | 2051 | .175 | .668 | .347 |

Figure 2 taken from Table II has as coördinates $-\log \gamma_{\pm}$ and $\sqrt{\mu}$. It may be seen that the points for any series of solvents, for example the series of nitric acid alone, or the series of nitric acid containing in addition one-tenth mole of glycine per 1000 g. of water, fall approximately on a straight line. These lines are not parallel. The activity coefficient of thallous chloride is depressed to a greater extent by tenth molal sodium hydroxide alone than by a similar solution to which glycine has been added. This may be due to formation of un-ionized thallous hydroxide in the more alkaline solution, for a plot of the conductivity of thallous hydroxide[5] according to the method of Onsager[6] indicates a considerable amount of association.

[4] "International Critical Tables," Vol. VII, p. 319.

[5] "International Critical Tables," Vol. VI, p. 243.

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

Solutions of glycine as strong as tenth molal depress the activity coefficient of thallous chloride by about 0.03. A change of this magnitude in $\gamma_{H^+}$ or $\gamma_{OH^-}$ would affect a $pK$ calculation appreciably only in very acid or in very alkaline solutions, and since most titration curves are determined in ampholyte solutions more dilute than tenth molal, one may conclude that, at least for glycine, this factor is negligible.

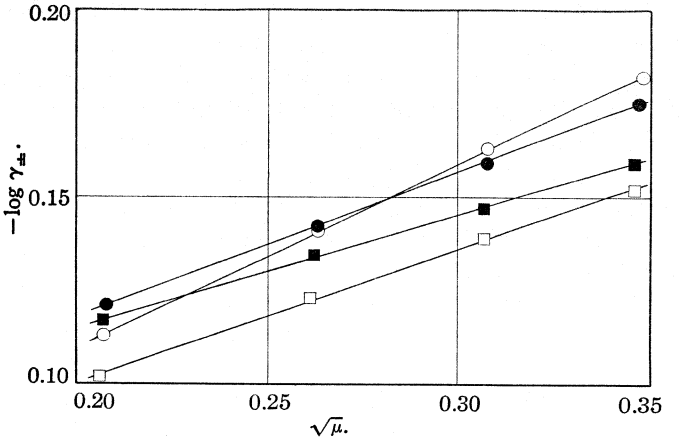


Fig. 2.—□, $HNO_3$; ○, NaOH; ■, glycine $M/10$ + $HNO_3$; ●, glycine $M/10$ + NaOH.

## Summary

The solubility of thallous chloride has been measured at 25° in the presence of glycine, of nitric acid, of sodium hydroxide, and of glycine to which acid or base has been added. The negative logarithm of the activity coefficient of thallous chloride is approximately a linear function of the glycine molality. It is approximately a linear function of the square root of the ionic strength in the solutions containing electrolytes as well.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

# THE ADSORPTION OF SILVER NITRATE BY FINELY DIVIDED SILVER

BY H. V. TARTAR AND OTTO TURINSKY

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There have been only a limited number of investigations showing the adsorption by a metal of its salts from aqueous solution. Patrick and Bachman[1] and Rosenberg and Stegeman[2] have studied the adsorption by mercury of the ions from solutions of mercuric salts. The most outstanding results are those reported by Euler and his co-workers[3] on the adsorption of silver nitrate by finely divided silver and silver foil. They report adsorption varying from 7.5 to 27.3% depending on the area of the silver surface and the concentration of the solution.

If silver adsorbs its salts to this degree, the potential of the silver electrode should be in part an adsorption potential. Furthermore, the potential of silver against its solution containing its ions would probably be very unsteady, and be influenced by the presence of gases such as oxygen.[4] But Lewis[5] has found the potential quite steady. He states, however, that plate silver has a more negative potential than silver in the finely divided state. The potential of the plate silver was more subject to change. One would be justified in the inference that these small differences might be due to adsorption of ions from solution.

The object of this investigation was the verification of the work of Euler and Hedelius. It was also contemplated, if marked adsorption occurred, to study the influence of gases such as oxygen, nitrogen, etc.

## Experimental Part

**Preparation of Solutions.**—All silver solutions were kept in carefully cleaned Pyrex bottles. In order to protect the solutions from the action of light, the bottles were covered with black, rubberized cloth and were kept in the dark. Such work as recrystallization, transfer of solutions, precipitation, evaporation, etc., was carried out in the presence of light only sufficient to permit experimental manipulation.

The silver nitrate used was a commercial "C. P. Analyzed" product which was recrystallized once and dried under reduced pressure at room temperature. Eight solutions were prepared varying in approximate normality from 0.1 to 0.0001. The quantitative analysis of these solutions is given with the adsorption experiments reported in Table I.

Solutions 1 and 2 were analyzed volumetrically with a solution of ammonium thio-

[1] Patrick and Bachman, *J. Phys. Chem.*, **30**, 134 (1926).

[2] Rosenberg and Stegeman, *ibid.*, **30**, 1306 (1926).

[3] Euler and Hedelius, *Arkiv. Kemi, Mineral. Geol.*, **7**, No. 31, 1716 (1920); Euler, *Z. Elektrochem.*, **28**, 446 (1922).

[4] Tartar and McClain, THIS JOURNAL, **53**, 3201 (1931).

[5] Lewis, *ibid.*, **28**, 158 (1906).

cyanate which had been carefully standardized by the use of recrystallized silver nitrate, c. p. silver wire, and pure electrolytic silver. Solutions 3, 5, 6 and 8 were analyzed gravimetrically.[6] For the analysis of solution 8, the most dilute, a 1000-cc. portion was required.

**Preparation of Finely Divided Silver.**—Silver was prepared by three different methods.

In the first method, silver carbonate was precipitated by adding sodium carbonate to a solution of silver nitrate. The precipitate was washed approximately thirty times with distilled water, dried at room temperature and reduced to silver in an atmosphere of hydrogen with very gentle heating. The product was analyzed volumetrically and found to be pure silver within the limits of experimental error.

This method is essentially the same as that used by Lewis[5] for the preparation of silver in the determination of the potential of the silver electrode.

The second method of preparation was that employed by Euler and Hedelius[3] in their experiments on adsorption by metallic powders. Precautions were taken to reproduce as nearly as possible this method of preparing silver in finely divided form. Silver chloride was prepared from silver nitrate and the former reduced by zinc under water. The excess zinc was then removed by treatment and decantation of a 10% sodium hydroxide solution. Each treatment with this solution was followed by three to four and sometimes ten to twelve decantations with water. It was necessary to extend this process over a week, involving sixteen treatments with sodium hydroxide. After the last treatment with sodium hydroxide, the product was thoroughly washed with water. The silver met the requirements of the qualitative test for purity suggested by Euler and Hedelius. A one-gram sample was first dissolved in nitric acid, the absence of a turbidity showing that no chloride was present. The silver was then precipitated as the chloride by adding hydrochloric acid and filtered. Sodium carbonate was added in slight excess to the filtrate. The absence of a turbidity after several hours' standing was assumed to indicate that the silver was zinc-free.

The third method was that used by Richards and Wells.[7] Ammonia gas was passed into 40–50 cc. of a freshly distilled formic acid. The acid was kept cool in an ice-bath to aid the formation of ammonium formate. The solution, which was distinctly acid, was then heated and 100 cc. of a solution containing 25 g. of silver nitrate was poured in slowly with stirring. Metallic silver was rapidly produced and was much finer and more spongy than that produced by the other two methods. It was washed about thirty times with water by decantation and dried at room temperature under reduced pressure. Careful analysis showed the metal to be pure within the limits of experimental error.

**Determination of Adsorption.**—The method for determining adsorption was carried out as follows. A carefully measured portion of silver nitrate solution was transferred to a Pyrex bottle containing a weighed amount of sponge silver. The mixture was well shaken and placed in a thermostat at 25° overnight. The silver settled easily, leaving a very clear supernatant liquid. A portion of the solution was then taken by means of a pipet and analyzed.

Dilute solutions were used in the greater portion of the experiments

[6] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 164. The samples were heated for a longer period and at a temperature not exceeding 100°.

[7] Richards and Wells, THIS JOURNAL, **27**, 475 (1905).

because any adsorption would be more apparent. The experimental data are reported in Table I.

TABLE I

RESULTS OF ADSORPTION EXPERIMENTS

| Expt. | Method of prepn. of silver | Silver used, g. | Soln. | $AgNO_3$ soln. for analysis, cc. | Silver soln. in contact with adsorbent, cc. | Silver in solution Before contact with adsorbent, g. | Silver in solution After contact with adsorbent, g. | Silver adsorbed g. |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1.0 | 1 | 25 | 50 | 0.5395 | 0.5395 | ..... |
| 2 | 1 | 1.0 | 2 | 50 | 150 | .6468 | .6477 | −0.0009 |
| 3 | 1 | 5.0 | 3 | 25 | 50 | .1075 | .1081 | − .0006 |
| 4 | 1 | 5.0 | 6 | 150 | 200 | .0214 | .0221 | − .0007 |
| 5 | 1 | 5.0 | 8 | 1000 | 1100 | .0161 | .0167 | − .0006 |
| 6 | 2 | 2.0 | 4 | 50 | 150 | .1609 | .1339 | + .027 |
| 7 | 2 | 2.0 | 6 | 150 | 250 | .0267 | .0142 | + .0125 |
| 8 | 3 | 5.0 | 5 | 50 | 150 | .0808 | .0798 | + .0010 |

**Discussion of Results.**—The data show no evidence of positive adsorption of silver nitrate by the silver metal. Experiments 2, 3, 4 and 5 show a small increase in the concentration of silver nitrate, indicating negative adsorption. Experiment 8 shows a small decrease in the concentration of the silver nitrate solution, indicating positive adsorption. The changes are slight and may be entirely due to experimental error. On the other hand, experiments 6 and 7, in which silver prepared according to Euler and Hedelius[3] was used, indicate marked adsorption, 16.8 and 46.8%, respectively.

The writers do not believe that this change is due to adsorption but rather to the reducing action of the small amount of zinc present. The removal of the last traces of zinc from sponge silver with 10% sodium hydroxide is difficult. Furthermore, the precipitation of zinc in alkaline solution with sodium carbonate is not a satisfactory test to establish the absence of zinc. The silver nitrate solutions obtained in experiments 6 and 7 were treated with hydrochloric acid in excess to precipitate the silver. Portions of these filtrates were tested with sodium carbonate for the presence of zinc but no precipitate formed after several days' standing. When samples of these same filtrates were treated with ammonium hydroxide and hydrogen sulfide a precipitate of zinc sulfide was formed almost immediately.

Euler[3] has also reported high adsorption of silver nitrate on silver foil, but careful scrutiny of the papers indicates that the foil used was not free from metals more active than silver. In fact, the statements indicate that Euler assumed that such impurities do not seriously affect adsorption measurements.

## Summary

1. A study has been made of the adsorption of silver salts by silver prepared by different methods. The results do not show positive adsorption.

2. The experimental work of Euler and Hedelius has been confirmed, but the writers present evidence to show that these results are due to the presence of zinc in the silver used.

SEATTLE, WASHINGTON

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 13]

# HEXAFLUORODISILANE[1]

BY WALTER C. SCHUMB AND E. LEE GAMBLE

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The only binary fluoride of silicon that has been definitely established up to the time of the present writing is the tetrafluoride, $SiF_4$. To be sure, H. St. C. Deville,[2] and Troost and Hautefeuille[3] reported the formation of substances which they believed to be subfluorides when (*a*) aluminum and silicon tetrafluoride were heated; (*b*) the gaseous tetrafluoride was passed over hot silicon; or (*c*) when a spark was passed through the tetrafluoride between silicon electrodes. The supposed subfluorides were described as gaseous, liquid, and solid.

In more recent times Jacquerod and Tourpaian,[4] working upon the density of silicon tetrafluoride, attempted to account for observed high values by the assumption that the passage of the gas over glass wool at red heat might have the effect reported by Troost and Hautefeuille, although the latter investigators passed the gas over elementary silicon at a much higher temperature. Furthermore, since no analyses either for silicon or fluorine were mentioned, and since the high densities referred to may be accounted for in several other ways, the evidence in favor of a subfluoride must be considered as based largely upon the work of the earlier experimenters.

Repetition of this work has failed to confirm the results claimed. Thus Ruff[5] states that he failed to obtain the subfluoride, of unknown composition, either by passage of the tetrafluoride over molten silicon and rapid cooling of the vapors, or by reduction of the tetrafluoride by graphite at 2000°, or by reduction with hydrogen; and Mellor[6] states that "the evidence for the existence of the subfluoride is not unimpeachable; and its composition is unknown."

[1] The present paper constitutes the detailed account of the work upon $Si_2F_6$ referred to in our communication to the Editor published in THIS JOURNAL, **53**, 3191 (1931).

[2] H. St. C. Deville, *Ann. chim. phys.*, [3] **49**, 76 (1857).

[3] Troost and Hautefeuille, *ibid.*, [5] **7**, 464 (1876).

[4] Jacquerod and Tourpaian, *J. chim. phys.*, **11**, 19 (1913).

[5] Ruff, "Die Chemie des Fluors," 1920, p. 119.

[6] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1925, Vol. VI, p. 934.

In spite of the negative character of the earlier work just referred to, the strong presumption remains that binary silicon fluorides other than the tetrafluoride should be capable of independent existence. This belief is strengthened by the fact that analogous compounds of carbon with fluorine have been prepared by Chabrié[7] and more recently have been referred to by Ruff.[8] Thus Chabrié prepared tetrafluoroethylene, $C_2F_4$, by heating silver fluoride and tetrachloroethylene in a sealed tube. Reactions were also observed by him to take place when hexachloroethane, $C_2Cl_6$, and hexachlorobenzene, $C_6Cl_6$, were separately heated in a sealed tube with silver fluoride, but the products formed were not identified. Ruff, in studying the reaction of various varieties of carbon with fluorine, has recently reported that, in addition to a very large proportion of carbon tetrafluoride, small quantities of less volatile products were condensed, which he believes contain such substances as hexafluoroethane, $C_2F_6$, and dodecafluorocyclohexane, $C_6F_{12}$. Further details concerning these products were promised by the authors.

In view of these facts, it is proposed to describe in this paper the preparation and some of the properties of hexafluorodisilane, $Si_2F_6$, together with other observations which have been made in this Laboratory during a study of the reaction of silicon with fluorine. The extension of this work to include the preparation of higher members of the series, $Si_nF_{2n+2}$, is now in progress.

It was decided to observe first whether when silicon burns in fluorine any product other than the tetrafluoride could be detected. The procedure followed was much the same as that previously described[9] in our study of sulfur hexafluoride, the fluorine generator being connected by copper tubing to a copper trap, cooled by a carbon dioxide–alcohol bath to about −78°, wherein any hydrogen fluoride was very largely condensed; then to a copper tube containing granular sodium fluoride to catch any remaining hydrogen fluoride. With reasonably dry electrolyte (KF·HF) the amount of hydrogen fluoride present in the gas after the generator has been operating a short time is very small, so that the provisions for removal of this gas proved to be more than adequate. The silicon employed was the crystalline variety, broken into small lumps, and was contained in a 2.54-cm. copper tube coupled to the rest of the apparatus. Inasmuch as the combination of silicon with fluorine is an intensely vigorous reaction, the copper tube was cooled externally with water from time to time. After leaving the reaction tube the gases passed through two glass condensing tubes, cemented to the copper with deKhotinsky cement, the first condenser being cooled with a carbon dioxide–alcohol mixture, the second with liquid air.

After a continuous run of fourteen hours, practically nothing had collected in the condenser at −78°, while about 200 g. of solid silicon tetrafluoride had been condensed by the liquid air. From the results of this preliminary experiment, it appeared probable that any fluorides less volatile than $SiF_4$, if formed, must be present in exceedingly small proportions. It is probable that the temperature in the zone of reaction is so high that any such compound would not be stable and with the rupturing of the Si–Si linkage

[7] Chabrié, *Compt. rend.*, **110**, 279 (1890); *Bull. soc. chim.*, [3] **7**, 18 (1892).

[8] Ruff and Keim, *Z. anorg. allgem. Chem.*, **192**, 249 (1930).

[9] Schumb and Gamble, THIS JOURNAL, **52**, 4302 (1930).

only $SiF_4$ would result. Rapid chilling of the gaseous products would favor the formation of such compounds and further experimentation along this line is anticipated.

Fluorine was next passed through the same apparatus over ferrosilicon containing 84.5% Si, with the aim of moderating the intensity of the reaction and of favoring the formation of silicon fluorides of higher molecular weight, but again the condenser, cooled to −78°, in which such fluorides would naturally be expected to be retained, yielded practically nothing.

It appeared to us probable, however, that the most promising method for the preparation of the fluorides derived from disilane, trisilane, etc., would be to start with the corresponding chlorides, $Si_2Cl_6$, $Si_3Cl_8$, etc., and to bring about replacement of chlorine by fluorine. This was in fact accomplished by warming together hexachlorodisilane, $Si_2Cl_6$, with anhydrous zinc fluoride, condensing and fractionating the products. The hexachlorodisilane was prepared by the chlorination of silicon alloys, such as "calcium silicon" and "calcium manganese silicon."[10] The temperature of the reaction tube containing the alloy was kept only high enough to maintain a continuous reaction—not far from 180°. From the crude product, yields of $Si_2Cl_6$ as high as 20 to 25% were obtained, considerably exceeding the yields reported by Martin,[11] who employed 50% ferrosilicon for this purpose.

For the preparation of hexafluorodisilane, "anhydrous" zinc fluoride was dried overnight at 110°, and to 100 g. of it contained in a dry Erlenmeyer flask was added 40 g. of freshly distilled $Si_2Cl_6$ (b. p. 145 ± 0.5°). The flask was sealed to two receivers, cooled by carbon dioxide–alcohol and by liquid air, respectively, and to a drying tube communicating with the outer air. Upon warming to 50–60°, a vigorous reaction was noted which, once started, continued without further application of heat for about one and one-half hours. Both receivers contained considerable quantities of white solids; that in the liquid air proved to be silicon tetrafluoride, which sublimed without residue. The other receiver contained a mixture of a small amount of unchanged $Si_2Cl_6$ together with about 9–10 g. of $Si_2F_6$, which was obtained from the mixture in a condition of purity by repeated sublimation. As the equilibrium pressure of this substance at room temperature is too great to permit preserving it safely in glass, the bulb containing it was kept cool throughout the subsequent work.

Hexafluorodisilane thus prepared is a colorless gas at ordinary temperatures, which instantly hydrolyzes in moist air with the formation of white solid hydrolysis products (see below); when cooled it condenses to snowy white crystals, which on warming, under slightly more than normal atmospheric pressure, melt to a colorless liquid.

**Vapor Pressure Measurements.**—The measurements of vapor pressure were carried out in the same apparatus and in the same manner as that described[9] in a former paper concerning sulfur hexafluoride, and the attainment of equilibrium pressures was insured by the agreement in the values observed with falling and with rising temperatures. About 8 g. of the resublimed material was taken at the start and the purity of the substance was tested by the constancy of the equilibrium pressures obtained after successive portions of the substance had been vaporized, as well as by the fact that the gas density determined upon the same material, as described below, remained constant for the first as well as for the very last portions to vaporize.

[10] Supplied us by the Electro Metallurgical Sales Corp., Niagara Falls. "Calcium-silicon" contained 30–35% Ca, 60–65% Si; "calcium-manganese-silicon" contained 17–18% Ca, 8–10% Mn, 55–60% Si.

[11] Martin, *J. Chem. Soc.*, **105**, 2836 (1914).

The vapor pressures of hexafluorodisilane, both as solid and as liquid, were determined over the range −79 to −4°. The temperatures were observed upon a toluene thermometer entirely immersed in the alcohol in the large Dewar tube thermostat; the thermometer had been checked by the Bureau of Standards at a number of points. Manometer readings, corrected to 0°, are recorded in Table I and the accompanying graph. It will be noted in the graph that the curve for the liquid was extended well into the supercooled region.

The melting point of the substance as determined by the intersection of the two branches of the vapor pressure curve agrees well with the direct observation of the temperatures of melting and solidification which were repeatedly carried out on the same material. The melting point of hexafluorodisilane, under the pressure of its own vapor, was thus found to be −18.7 ± 0.1°.

TABLE I

VAPOR PRESSURE OF HEXAFLUORODISILANE

| Experimental data | | | | Interpolated from graph | | |
|---|---|---|---|---|---|---|
| Corr. emp., °C. | Corr. press., mm. | Corr. temp., °C. | Corr. press., mm. | | Temp., °C. | Corr. press., mm. |
| −78.9 | 3.0 | −19.4 | 738.4 | | −75 | 3 |
| −60.7 | 13.5 | −18.9 | 773.2 | | −70 | 5 |
| −59.2 | 15.5 | −19.4 | 755.7 | | −65 | 7 |
| −51.3 | 37.9 | −20.1 | 731.5 | | −60 | 14 |
| −50.2 | 42.8 | −20.6 | 720.8 | | −55 | 25 |
| −45.1 | 73.7 | −21.1 | 693.4 | | −50 | 45 |
| −44.6 | 77.2 | −21.9 | 662.6 | | −45 | 77 |
| −37.5 | 152.4 | −22.5 | 644.2 | | −40 | 125 |
| −36.6 | 175.8 | −24.1 | 592.7 | [a] | −35 | 197 |
| −32.8 | 237.5 | −24.6 | 576.5 | | −30 | 304 |
| −32.4 | 247.5 | −25.1 | 561.6 | | −25 | 467 |
| −29.5 | 319.6 | −25.6 | 544.4 | | −20 | 703 |
| −27.8 | 367.0 | −26.5 | 515.8 | | −15 | 937 |
| −25.6 | 448.5 | −27.5 | 487.7 | | −10 | 1195 |
| −25.1 | 464.8 | −28.0 | 456.5 | | − 5 | 1505 |
| −24.9 | 492.0 | −18.6 | 779.6 | | | |
| −23.7 | 528.8 | −18.5 | 784.6 | | | |
| −23.4 | 537.3 | −18.3 | 794.5 | | | |
| −22.4 | 589.5 | −18.1 | 804.0 | | | |
| −22.3 | 595.0 | −17.1 | 839.3 | | | |
| −21.4 | 631.8 | −15.1 | 929.9 | | | |
| −20.4 | 680.1 | −12.6 | 1048.9 | | | |
| −20.3 | 685.1 | − 9.6 | 1217.8 | | | |
| −20.2 | 692.6 | − 6.5 | 1402.1 | | | |
| | | − 3.7 | 1579.3 | | | |

[a] Region of supercooled liquid. Pressures throughout are for mercury at 0°.

From the graph, the temperature at which the vapor pressure of this substance becomes 760 mm. is found to be −19.1°, that is, very slightly below

its melting point, a circumstance that is not uncommon among fluorides of this type.

**Gas Density.**—The formula, $Si_2F_6$, was checked by four determinations of the density of the substance in the gaseous condition, whence the molecular weight could be calculated approximately. The densities were

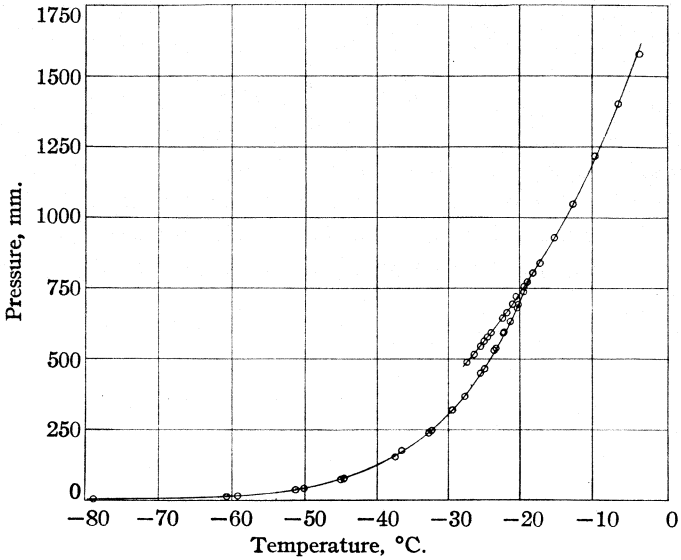


Fig. 1.

determined by observing the gain in weight of an evacuated glass globe (volume, before evacuation, 495.58 cc.) when filled with the gas at a known pressure and temperature. The weighings were done by the counterpoise method, and the precautions and corrections customary in such work were observed.

GAS DENSITY RESULTS

| Corr. pressure, mm. at 0° | Temp., °C. | Wt. of gas, g. | Mol. wt. |
|---|---|---|---|
| 702.6 | 21.4 | 3.2842 | 173.2 |
| 754.6 | 20.0 | 3.5658 | 174.2 |
| 753.9 | 20.0 | 3.5654 | 174.5 |
| 306.7 | 24.8 | 1.4175 | 173.2 |

The calculated molecular weight is in sufficiently close agreement with the theoretical value for $Si_2F_6$, 170.1, to serve as a check upon the composition of the substance. The mean value of the density of the gas at 0°, 760 mm., calculated from the data given, is 7.759 g. per liter; the relative density referred to air being 5.997, assuming the average molal weight of air to be 28.98.

**Hydrolysis.**—The hydrolysis of hexafluorodisilane differs sharply

from that of silicon tetrafluoride in that hydrogen gas is formed as one product. Other products are 1,2-bis-(oxy-oxo)-disilane, or "silico-oxalic acid," $H_2Si_2O_4$, fluosilicic acid, $H_2SiF_6$, and silicic acid. Quantitative evidence was sought in order to establish a reasonable hypothesis for the mechanism of the hydrolysis. The experiments, which will be briefly described, lead us to believe that the hydrolytic action consists of three consecutive reactions, as follows

$$Si_2F_6 + 4H_2O \longrightarrow 6HF + H_2Si_2O_4 \quad (1)$$
$$6HF + H_2Si_2O_4 \longrightarrow H_2 + H_2SiF_6 + H_4SiO_4 \quad (2)$$
$$H_4SiO_4 + 6HF \longrightarrow 4H_2O + H_2SiF_6 \quad (3)$$

Corroborative evidence of reaction (2) is found in the fact that "silico-oxalic acid," when separately treated with hydrofluoric acid, yields hydrogen. The extent to which the separate reactions proceed will depend upon such conditions as the temperature, time of contact, quantity of water employed, etc.

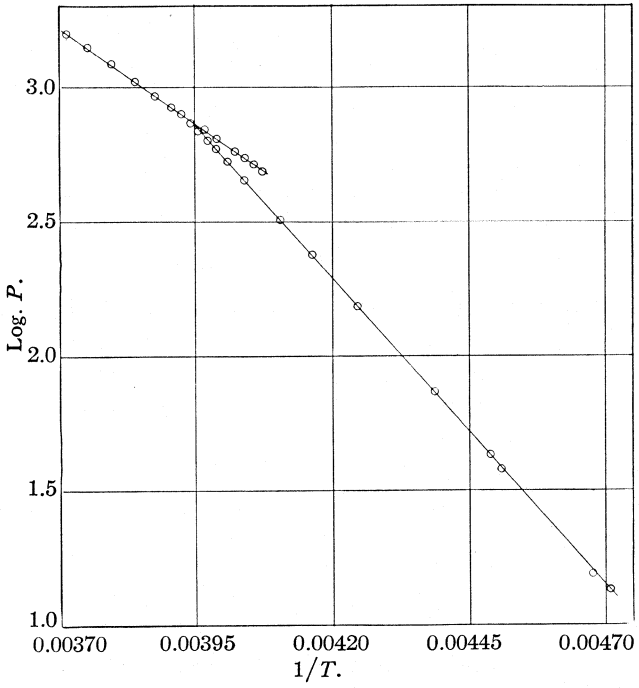


Fig. 2.

Cylindrical glass bulbs (volume approximately 120 cc.), supplied with stopcocks at each end, were evacuated and gaseous hexafluorodisilane was admitted, the weight of gas being determined by the gain in weight of the bulb, using a similar glass counterpoise. One end of the bulb was now dipped into distilled water; in one case previously chilled water was used, in two other trials the water was at room temperature. On opening the

lower stopcock and slightly cooling the upper part of the bulb water was drawn into the bulb and the gas instantly hydrolyzed with the separation of a white solid. When about 30 cc. of water had entered, the lower cock was closed and the bulb shaken for some time so as to obtain thorough mixing of the contents.

The hydrolysis products contained in the bulb were examined as follows. The gaseous portion was drawn over into a gas buret and proved to be hydrogen. The bulb was next broken open and the liquid contents filtered; the solid residue consisting mainly of silicic acid was dried and ignited to $SiO_2$. The filtrate was treated with a known weight of potassium chloride and alcohol was added in volume equal to that of the solution, thereby precipitating the fluosilicate as $K_2SiF_6$, which was filtered off, dried at 110° and weighed; the chloride thus introduced was later recovered quantitatively as silver chloride, thus indicating the absence of any appreciable quantity of chloride in the original hexafluorodisilane. In a typical experiment, 0.8420 g. of the gas on hydrolysis and subsequent treatment as already described, yielded 86.8 cc. of hydrogen (reduced to dry basis, 0°, 760 mm.); a total of 0.3592 g. $SiO_2$; 0.9280 g. $K_2SiF_6$; and no chloride. These data are in reasonable agreement with the series of reactions given, and the assumption that, while reaction (1) proceeds very rapidly to completion, only about 80% of the "silico-oxalic acid" formed reacts with HF according to (2)—the rest of the HF reacting in (3) with some of the silicic acid liberated in (2).

**Analysis.**—The elementary analysis of hexafluorodisilane proved to be somewhat troublesome, but the method finally employed yielded very satisfactory results. A known weight of the substance, which had been repeatedly sublimed, was introduced into a well-evacuated glass bulb which was provided with a stopcock at each end; the gain in weight of the bulb, which had a volume of about 65 cc., gave the weight of the sample. The bulb was now connected at one end with a source of dry nitrogen and at the other end with a tube ending in a funnel-shaped opening which dipped below the surface of distilled water in a beaker. The gas within the bulb was now swept out at a very slow rate by the stream of nitrogen into the water and was hydrolyzed thereby instantly and completely. The water was kept stirred so that the surface did not become caked over with solid hydrolysis products. The sweeping process was continued for about half an hour, which proved to be adequate for the complete displacement of the gaseous fluoride.

The contents of the beaker were filtered and the filter was thoroughly washed; the filtrate, containing hydrofluoric and fluosilicic acids, was titrated with standard, carbonate-free alkali (0.4972 *N* NaOH), using phenolphthalein as an indicator. Hereby not only the hydrofluoric acid but also the fluosilicic acid is quantitatively converted into sodium fluoride

$$H_2SiF_6 + 6NaOH = 6NaF + H_4SiO_4 + 2H_2O$$[12]

From the results of this titration the percentage of fluorine in the sample was calculated.

The silicon in the sample was determined as $SiO_2$; the bulk of this was obtained by collecting, drying and igniting the solid hydrolysis products—silicic acid and 1,2-bis-(oxy-oxo)-disilane—or "silico-oxalic acid"; the rest was obtained by evaporating the filtrate, after neutralization with alkali as above described, baking the residue at 115°, leaching out the soluble matter, filtering, drying and igniting the silica. From the combined weights of silica the percentage of silicon in the sample was calculated.

[12] The validity of this method, which was employed by Sahlbom and Hinrichsen [*Ber.*, **39**, 2609 (1906)], was demonstrated by separate experiments made with pure sodium fluosilicate, which it was found may be quantitatively converted into the fluoride by titration with 0.5 *N* alkali, using phenolphthalein as an indicator.

THE ESSENTIAL DATA AND RESULTS

| Sample, g. | 0.4972 *N* NaOH used, cc. | Total $SiO_2$, g. | F, % | Si, % |
|---|---|---|---|---|
| 0.4635 | 32.76 | | 66.77 | |
| .4616 | 32.65 | | 66.82 | |
| .4652 | | 0.3223 | | 32.37 |
| .4625 | | .3243 | | 32.76 |
| | | Theory for $Si_2F_6$ | 67.01 | 32.99 |

In conclusion, it seemed to us important to determine whether the reaction employed to produce hexafluorodisilane could be applied in an analogous manner to the preparation of the corresponding fluoride of carbon, $C_2F_6$, which, as stated above, Chabrié[7] very probably had first prepared by heating silver fluoride with hexachloroethane in a sealed tube. In this case, however, unsatisfactory results were obtained at ordinary pressure with anhydrous zinc fluoride and hexachloroethane, because when heated together in a flask, the chloride sublimes unchanged; when the vapors of the chloride were passed over zinc fluoride contained in a large graphite boat inside a Pyrex tube at 250–300° the same results were obtained; and when higher temperatures (400–450°) were used partial decomposition of the chloride occurred, yielding chlorine and tetrachloroethylene, as well as a large amount of unchanged original chloride, but no detectable amount of volatile fluoride. A solution of hexachloroethane in diphenyl, refluxed with zinc fluoride at the boiling point of the solution, likewise failed to give the desired results. Further experimentation is planned along these lines, especially under increased pressure.

## Summary

1. Hexafluorodisilane, $Si_2F_6$, has been prepared by gently warming hexachlorodisilane with anhydrous zinc fluoride, followed by condensation and fractionation of the products.

2. This substance is gaseous under ordinary conditions of temperature and pressure, but may be condensed to a white solid melting at −18.7° under 780 mm. pressure. The vapor pressures of the substance as solid and liquid have been determined from −79 to −4°; the vapor pressure becomes 760 mm. at −19.1°.

3. The molecular weight, 173.8, calculated from gas density determinations, agrees reasonably well with the theoretical for $Si_2F_6$ (170.1).

4. The hydrolysis of this substance yields hydrogen, silicic acid, fluosilicic acid, 1,2-bis-(oxy-oxo)-disilane or "silico-oxalic acid" and some hydrofluoric acid. The mechanism of this process, which was studied quantitatively, is discussed.

5. The preparation of hexafluoroethane by the interaction of hexachloroethane and zinc fluoride has failed to give satisfactory results under ordinary pressure.

6. In the preliminary preparation of hexachlorodisilane greatly improved yields were obtained by the chlorination of calcium–silicon alloys or calcium–manganese–silicon alloys in place of ferrosilicon.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RADCLIFFE COLLEGE]

# A REVISION OF THE ATOMIC WEIGHT OF LANTHANUM. I. THE ANALYSIS OF LANTHANUM BROMIDE. II. THE SPECIFIC GRAVITIES OF LANTHANUM CHLORIDE AND BROMIDE. III. THE INCREASED EFFICIENCY OF CALCIUM BROMIDE AS A DRYING AGENT AT LOW TEMPERATURES

BY GREGORY PAUL BAXTER AND EVELYN EMMA BEHRENS

RECEIVED OCTOBER 23, 1931 PUBLISHED FEBRUARY 5, 1932

The atomic weight of lanthanum in current use, 138.90,[1] is based on two series of analyses of anhydrous lanthanum chloride by Baxter, Tani and Chapin,[2] and Hopkins and Driggs.[3] Since the concordance of neither series of determinations was all that could be desired, we have continued the work of the former authors by further purification of the material used and by analyzing the anhydrous bromide. This work has yielded a value slightly higher than the one given above, 138.926, and more nearly in accord with Aston's finding that lanthanum is a simple element.[4]

**Purification of Reagents.**—Water and nitric acid were purified by distillation. Oxalic acid was three times crystallized, the first time after the addition of a small amount of nitric acid. Bromine was purified by the method already described.[5]

In the dehydration of lanthanum bromide in a current of hydrogen bromide described later the hydrogen bromide was collected in pure water and the solution was oxidized with a slight deficiency of permanganate for the recovery of the bromine. Since neither chloride nor organic matter were introduced in the process, the recovered material was of the same degree of purity as the original.

Hydrogen bromide was prepared with the apparatus shown in Fig. 1. Electrolytic hydrogen from the cells A, containing zinc amalgam–hydrochloric acid–platinized platinum, was passed over fused potassium hydroxide in the towers B and bubbled through bromine in the flask C at about 44° before passing over hot platinized asbestos in D. If a solution of the gas was desired it was passed through E into pure water. To obtain dry gas it was bubbled through ferrous bromide solution in G and H to remove traces of bromine and dried by means of fused calcium bromide in J. Before use the solution was fractionally distilled with a quartz condenser, with rejection of the head and tail portions. A colorless product resulted.

[1] Report of the Committee on Atomic Weights of the International Union of Chemistry, THIS JOURNAL, **53**, 1627 (1931).

[2] Baxter, Tani and Chapin, *ibid.*, **43**, 1080 (1921); **44**, 328 (1922).

[3] Hopkins and Driggs, *ibid.*, **44**, 1927 (1922).

[4] Aston, *Nature*, **113**, 856 (1924).

[5] Baxter and Ishimaru, THIS JOURNAL, **51**, 1730 (1929).

The silver was a portion of that purified by Professor S. Ishimaru in connection with an earlier research on the atomic weight of meteoric nickel.[6] Standard methods of purification were used and the product has been found in other investigations to be exactly similar to other samples similarly prepared.

Nitrogen was obtained by passing air through concentrated ammonia in L (Fig. 1), over hot copper catalyst in M, through dilute sulfuric acid in N, and over silver nitrate solution, potassium hydroxide solution, fused potassium hydroxide, concentrated sulfuric acid and resublimed phosphorus pentoxide in O and P. It contained argon and hydrogen (from catalytic decomposition of ammonia in M). Air was purified and dried by passing over similar reagents in Q and R.

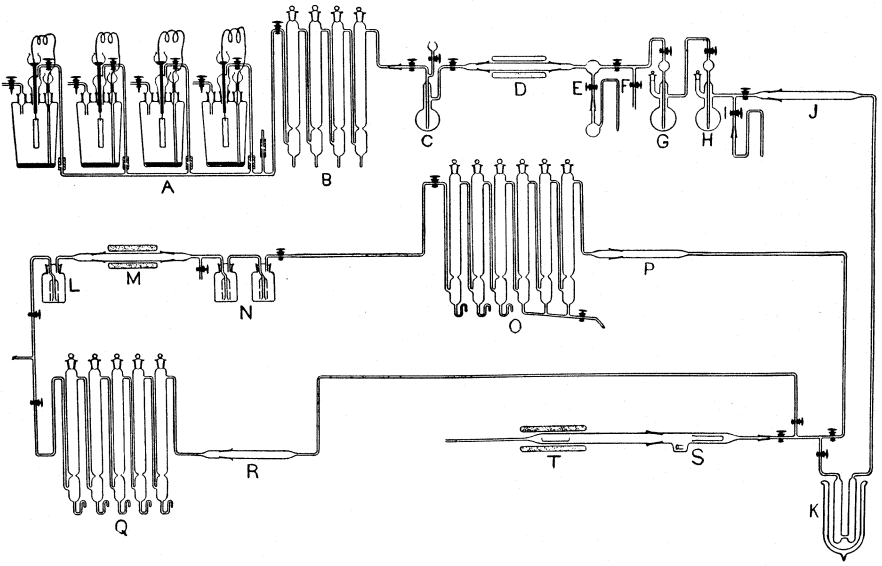


Fig. 1.

**The Purification of Lanthanum Material.**—The starting point in the purification was two series of less soluble fractions obtained by Chapin and by Tani in the fractional crystallization of lanthanum ammonium nitrate. This is one of the most favorable cases of purification of a rare earth by fractional crystallization because lanthanum tends to concentrate alone in the least soluble fraction, with cerium, praseodymium, neodymium and other rare earth elements following in the more soluble fractions in that order.[7] Fractions from the two series of estimated similar purity were combined, and the crystallization as double ammonium nitrate was continued.

[6] Baxter and Ishimaru, THIS JOURNAL, **51**, 1730 (1929).

[7] Auer v. Welsbach, *Sitzungsb. Acad. Wiss. Wien*, **112**, 1043 (1903).

In the fractionation by Chapin, ninety-six series of crystallizations were carried out, involving 2300 fractions. The final series contained 39 fractions. In that carried out by Tani also ninety-six series of crystallizations, involving 1100 fractions, were completed. In the final series there were twelve fractions. Rejection of the least soluble fraction was more liberally adopted in the latter fractionation, which permitted the greater limitation of the number of fractions.

The combination of the fractions of the two final series is indicated in the following table, in which the less soluble fractions are given the lower numbers.

| Tani | Chapin | Baxter and Behrens |
|---|---|---|
| 1 | 1, 2 | 1 |
| 2, 3 | 3, 4 | 2 |
| 4 | 5, 6 | 3 |
| 5 | 7, 8 | 4 |
| 6 | 9, 10 | 5 |
| 7 | 11, 12 | 6 |
| 8 | 13, 14 | 7 |
| 9 | 15, 16 | 8 |
| 10 | 17, 18 | 9 |
| 12 | 19, 21 | 10 |

None of the fractions even in concentrated solution in a 5-cm. layer showed any indication of absorption bands so that the essential absence of praseodymium and neodymium was assured at the outset. Detectable amounts of cerium, however, were contained in the more soluble fractions, and it was for the removal of these that the purification process was intended.

The fractionation scheme which was carried out is understood best from Fig. 2 in which the lowest number in a series represents the least soluble fraction. Rejected mother liquors are shown at the right of a series by diagonal lines unconnected with any number. When the least soluble fraction became small it was set aside to be combined later with a least soluble fraction of a subsequent series as indicated by lines in the diagram. Thirty series of fractional crystallizations were completed, the total number of individual crystallizations being 383. Thirteen fractions resulted in the final series, numbered 371 to 383. The final series of fractions was tested for cerium by boiling the solutions with ammonium persulfate,[8] with the addition of enough ammonium hydroxide to keep the solution barely on the acid side of neutrality. The precipitates formed always contained a small amount of lanthanum hydroxide colored yellow by the ceric hydroxide when cerium was present.

The most soluble fraction, 382, yielded a small amount of cerium. Fraction 379 yielded a trace. The mother liquor of fraction 376 gave no visible indication of cerium. The arc spectra of fractions 371, 372, 376 and 379, after removal of cerium as described, were carefully compared, using pure graphite electrodes and a Féry quartz spectrograph. No differences could be detected, and the arc lines of cerium were not detectable in the spectrograms. Since even 1% of cerium would raise the apparent

[8] Witt and Thiel, *Ber.*, **33**, 1315 (1900).

atomic weight of lanthanum by only 0.01 unit, the purity of the less soluble fractions was undoubtedly sufficient for the purpose. This conclusion is supported by the results of the analyses of bromide prepared from these fractions, for the differences found were no larger than could be attributed to unavoidable experimental error.

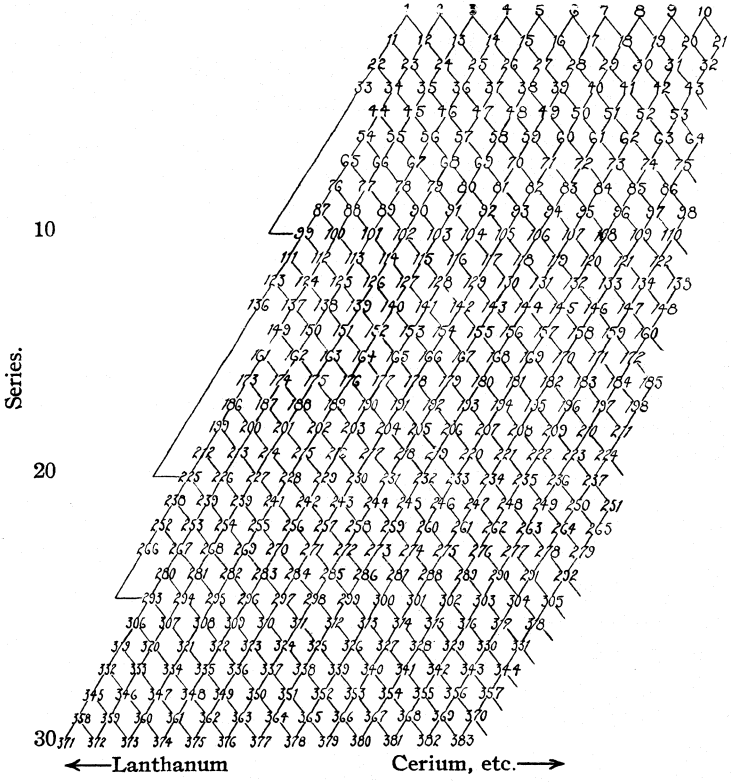


Fig. 2.

**The Preparation of Lanthanum Bromide.**—Fractions 371, 372, 376 and 379 were selected for the preparation of lanthanum bromide. A filtered solution of the double nitrate was made strongly acid with nitric acid and the oxalate was precipitated by the addition of a solution of an excess of oxalic acid. After washing by decantation the precipitate was collected on a disk of filter paper in a large porcelain Gooch crucible and dried. Ignition at dull redness in a platinum boat in a porcelain muffle followed. Solution in nitric acid, precipitation as oxalate, and ignition was then twice repeated. The ignited mixture of oxide and carbonate was pure white.

To prepare the bromide the oxide was dissolved in hydrobromic acid in a quartz dish and the solution was evaporated to saturation. After cooling

the crystals were centrifugally drained and washed and then were three times recrystallized in platinum. The crystals were preserved in quartz dishes over fused potassium hydroxide.

**The Dehydration of Lanthanum Bromide.**—Owing to the danger of the formation of basic salt, the drying of the lanthanum bromide was carried out with the greatest care. Matignon[9] first pointed out that in the dehydration of the rare earth chlorides a neutral product could only be obtained by a thorough preliminary dehydration followed by fusion in an atmosphere of dry hydrogen chloride. Baxter and Chapin,[10] and Baxter and Stewart[11] applied this principle successfully in the preparation of neodymium and praseodymium chloride and the procedure has since been followed by others. It is especially important that as much as possible of the water of crystallization be eliminated by efflorescence before any attempt is made to fuse the salt.

In view of this experience the following method was employed. The hydrated crystals were placed in a weighed platinum boat contained in the quartz tube of a Richards bottling apparatus (T and S, Fig. 1) and the tube was heated to about 110° by means of an aluminum block oven,[12] while at the same time a current of nitrogen containing a small amount of hydrogen bromide was passed through the tube. Since the inversion temperature of the heptahydrate was found experimentally to be 117°, there was no danger of melting. The crystal water evaporated slowly, a period of eight to ten hours being necessary before there was visible evidence of the end of the first stage in the dehydration. Judging from analogy with the chlorides, one molecule of crystal water still remained. Pure hydrogen bromide was then passed through the tube and the temperature was maintained at about 160° until the residual crystal water had evaporated. Again the temperature was raised, to 300°, for some time. Next the aluminum oven was removed and replaced by an electrically heated sleeve. The temperature was raised to dull redness for a short time and finally the salt was fused, at bright redness, as rapidly as possible. Experience with praseodymium chloride has shown that prolonged fusion is highly undesirable, probably because of traces of water in the gas stream. As soon as fusion was complete the salt was allowed to solidify the hydrogen bromide was displaced by nitrogen and this in turn by air. The boat was then transferred to the weighing bottle in which it had originally been weighed, by means of the bottling apparatus, the stopper was inserted and the weighing bottle and contents were placed in a desiccator preparatory to weighing.

[9] Matignon, *Compt. rend.*, **133**, 289 (1901).

[10] Baxter and Chapin, THIS JOURNAL, **33**, 17 (1911).

[11] Baxter and Stewart, *ibid.*, **37**, 529 (1915).

[12] Baxter and Coffin, *Proc. Am. Acad.*, **44**, 184 (1909).

Except in two preliminary exploratory experiments in which the technique had not been perfected, the fused salt gave a perfectly clear solution when dissolved in a minimum amount of water. We interpret this to mean the absence of basic salt, although if the latter possesses appreciable solubility the conclusion is not justified. In order to throw more light on this important question, after the first two analyses the drying of the hydrogen bromide was made more complete. Baxter and Warren[13] have shown that fused calcium bromide leaves 0.2 mg. of moisture per liter in air which has been passed over it at room temperature. Most of the better drying agents such as phosphorus pentoxide and sulfuric acid contaminate the hydrogen bromide with decomposition products. We therefore attempted to increase the efficiency of calcium bromide by lowering its temperature. This was done by inserting in the hydrogen bromide train the U-tube K filled with fused calcium bromide and cooling this tube with solid carbon dioxide–alcohol mixture. In a following section is given experimental evidence that this expedient is highly successful in increasing the efficiency of the drying. Since the later experiments with lanthanum bromide showed no difference from the earlier ones, it seems likely that residual water in the hydrogen bromide did not affect the early experiments.

**The Analysis of Lanthanum Bromide.**—The analysis of the bromide followed conventional lines. The solution was diluted to a volume of 1000 to 1500 ml. so that the concentration was less than 0.05 normal. Baxter and Greene[14] have recently pointed out that a concentration as low as this is desirable to avoid occlusion by silver bromide. A quantity of silver very nearly equivalent to the bromide was carefully weighed and dissolved in nitric acid with especial precautions to avoid loss of spray, and the solution was diluted to a volume of about one liter. The silver solution was then added in small portions with gentle agitation to the bromide solution in a glass-stoppered flask, and the mixture was occasionally shaken for a week. A nephelometric test for excess of bromide or silver was then made. Any deficiency found was made up by adding hundredth normal solution, and the shaking and testing repeated until the exact end-point was reached. All the analyses were then allowed to stand undisturbed during the summer months and then were again shaken and tested. In the first and fifth analyses a change amounting to only 0.1 mg. of silver was observed. The others remained unchanged.

In order to determine the silver bromide an excess of a few mg. of silver was added to each analysis to reduce the solubility of silver bromide and after standing for some time the precipitates were thoroughly washed and collected on weighed platinum sponge crucibles. In analyses 6 to 8 the washing liquid contained 2 mg. of silver per liter and the precipitate was

[13] Baxter and Warren, THIS JOURNAL, **33**, 340 (1911).

[14] Baxter and Greene, *ibid.*, **53**, 611 (1931).

transferred to the crucible with pure water. In analyses 9 and 10 the washing as well as the transference was done with water. Drying at 300° for eighteen hours was followed by weighing. In analyses 6 to 8 the crucibles and contents were again heated just above the melting point of the silver bromide. A slight loss in weight was presumably due to retained moisture. In analyses 9 and 10 the bulk of the silver bromide was transferred to a quartz crucible and the loss in weight on fusion determined. The moisture determinations made in the latter way showed no difference from those made in the former.

The solubility of silver bromide in the filtrate and silver nitrate washings was assumed to be negligible but a correction of 0.1 mg. per liter was applied for the aqueous washings. The precipitating flask was rinsed with ammonia to collect silver bromide which had escaped transference and the bromide content of this solution determined nephelometrically. This correction amounted to 0.1 mg. per analysis on an average. A negative correction was applied for any bromide added during the adjustment of the end-point.

Weighings were made on a balance sensitive to 0.01 mg. with weights which had been carefully standardized. All weighings were made by substitution, with the use of similar counterpoises in the case of the weighing bottles and crucibles. Electrostatic charges were eliminated by means of a small amount of radium salt in the balance case. Vacuum corrections were applied as follows:

| | Specific gravity | Vacuum correction per g., mg. |
|---|---|---|
| Weights | 8.3 | |
| Silver | 10.49 | −0.031 |
| Silver bromide | 6.47 | +0.041 |
| Lanthanum bromide | 5.06 | +0.091 |

The determination of the density of lanthanum bromide is described in a later part of this paper.

TABLE I

THE ATOMIC WEIGHT OF LANTHANUM

Series I. $LaBr_3 : 3Ag$

Ag = 107.880 Br = 79.916

| No. of analysis | Fraction | Weight of $LaBr_3$ in vacuum, g. | Wt. of Ag in vacuum, g. | Wt. of Ag added or subtracted, g. | Corr. wt. of Ag in vacuum, g. | Ratio $LaBr_3$:3Ag | Atomic weight of lanthanum |
|---|---|---|---|---|---|---|---|
| 1 | 376 | 4.01090 | 3.42980 | −0.00179 | 3.42801 | 1.170037 | 138.923 |
| 2 | 379 | 5.19186 | 4.43757 | −0.00030 | 4.43727 | 1.170057 | 138.929 |
| 3 | 372 | 6.57727 | 5.62165 | −0.00032 | 5.62133 | 1.170056 | 138.929 |
| 4 | 371 | 6.38414 | 5.45632 | −0.00020 | 5.45612 | 1.170088 | 138.939 |
| 5 | 372 | 6.91830 | 5.91257 | +0.00030 | 5.91287 | 1.170061 | 138.931 |
| 6 | 371 | 6.19359 | 5.29319 | +0.00020 | 5.29339 | 1.170041 | 138.924 |
| | | | | | Average | 1.170057 | 138.929 |

TABLE I (*Concluded*)

Series II. $LaBr_3$ : 3AgBr

| No. of analysis | Fraction | Weight of $LaBr_3$ in vacuum, g. | Wt. of AgBr in vacuum, g. | Dissolved AgBr, g. | Loss in wt. on fusion, g. | Corr. wt. of AgBr in vacuum, g. | Ratio $LaBr_3$:3AgBr | At. wt. of lanthanum |
|---|---|---|---|---|---|---|---|---|
| 7 | 376 | 4.01090 | 5.96768 | 0.00000 | 0.00025 | 5.96743 | 0.672132 | 138.923 |
| 8 | 379 | 5.19186 | 7.72480 | .00000 | .00005 | 7.72475 | .672107 | 138.909 |
| 9 | 372 | 6.57727 | 9.78513 | .00035 | .00000 | 9.78548 | .672146 | 138.931 |
| 10 | 371 | 6.38414 | 9.49818 | .00030 | .00005 | 9.49843 | .672126 | 138.920 |
| 11 | 372 | 6.91830 | 10.29255 | .00040 | .00010 | 10.29285 | .672146 | 138.931 |
| | | | | | | Average | .672131 | 138.923 |
| | | | | | | Average of Series I and II | | 138.926 |

Below the results are arranged by fractions of the lanthanum material.

| | $LaBr_3$:3Ag | $LaBr_3$:3AgBr | Average |
|---|---|---|---|
| 371 | 138.939 | 138.920 | |
| | 138.924 | | 138.928 |
| 372 | 138.929 | 138.931 | |
| | 138.931 | 138.931 | 138.931 |
| 376 | 138.923 | 138.923 | 138.923 |
| 379 | 138.929 | 138.909 | 138.919 |

The extreme difference in the experimental ratios amounts to 0.005% in both series, corresponding to 0.25 mg. of silver and 0.40 mg. of silver bromide. Although there is a slight apparent trend downward with increasing solubility of the double nitrate fractions, it is doubtful whether this represents a real difference in the material especially since the most probable impurity, cerium, would raise, not lower, the observed atomic weight.

The ratios of silver used to silver bromide obtained in the same analysis fall within the experimental limit to be expected in analyses of this type and indicate that the silver bromide was reasonably free from contamination.

| Analysis | Ag:AgBr |
|---|---|
| 1 and 7 | 0.574453 |
| 2 and 8 | .574422 |
| 3 and 9 | .574456 |
| 4 and 10 | .574423 |
| 5 and 11 | .574464 |
| Average | .574444 |
| Theoretical | .574453 |

The results of the recent analyses of lanthanum halides are summarized below.

| | | |
|---|---|---|
| Baxter, Tani and Chapin | $LaCl_3$:3Ag | 138.916[a] |
| | $LaCl_3$:3AgCl | 138.915[a] |
| Hopkins and Driggs | $LaCl_3$:3Ag | 138.89 |
| Baxter and Behrens | $LaBr_3$:3Ag | 138.929 |
| | $LaCl_3$:3AgBr | 138.923 |

[a] Corrected for the new specific gravity of lanthanum chloride found as described in a later part of this paper, 3.842.

The average value obtained in the two investigations in this Laboratory, 138.92, is higher than the International value by 0.02 unit.

## II. THE SPECIFIC GRAVITIES OF LANTHANUM CHLORIDE AND BROMIDE

For the purpose of finding the buoyant effect of the air on anhydrous lanthanum bromide in the preceding investigation, a knowledge of the density of this salt was necessary. Since the evidence concerning the density of the anhydrous chloride is conflicting, the densities of both salts were determined, by displacement of toluene.

Toluene was dried over sodium and fractionally distilled, with rejection of the first and last fifth, although the boiling point was constant within a degree. Its density was determined at 25° both with an Ostwald pycnometer and also with the special pycnometer for solids described by Baxter and Hines.[15] The latter consisted of a weighing bottle provided with two stoppers, one of which was of ordinary shape and was used during the weighing of the dry substance. Into the other were sealed two glass capillaries which served to fill the bottle with liquid. When the bottle was filled with liquid the joint was made tight with weighed amounts of sirupy phosphoric acid or grease.

Lanthanum bromide was dehydrated and fused in a platinum boat as described in the preceding paper, and was weighed in the pycnometer bottle with the ordinary stopper. The salt was then quickly covered with toluene and placed in a vacuum desiccator in which the pressure was reduced until the toluene boiled gently. As soon as air had thus been expelled from the salt the pycnometer stopper provided with a weighed amount of sirupy phosphoric acid as lubricant was inserted and the pycnometer was filled with toluene at 25°. From the weight of the pycnometer filled with toluene and containing the boat and salt, and the weight similarly determined with the empty boat, the toluene displaced was found.

Lanthanum chloride was prepared from the oxide of fraction 376 and was several times crystallized. It was dehydrated and fused as described by Baxter, Tani and Chapin,[16] and its density found as described above with the bromide.

The following vacuum corrections have been applied:

| | Density | Vacuum correction per gram |
|---|---|---|
| $LaBr_3$ | 5.06 | +0.00009 |
| $LaCl_3$ | 3.84 | +0.00017 |
| Toluene | 0.8613 | +0.00126 |
| Water | 0.9971 | +0.00106 |

[15] Baxter and Hines, *Am. Chem. J.*, **31**, 220 (1904).

[16] Baxter, Tani and Chapin, THIS JOURNAL, **43**, 1080 (1921).

OSTWALD PYCNOMETER

| | Weight of water in vacuum, g. | Weight of toluene in vacuum, g. | Density of toluene 25°/4° |
|---|---|---|---|
| | 9.85588 | 8.51362 | |
| | 9.85584 | 8.51347 | |
| Average | 9.85586 | 8.51355 | 0.86129 |

SPECIAL PYCNOMETER

| | | | |
|---|---|---|---|
| | 11.55863 | 9.98437 | |
| | 11.55863 | 9.98408 | |
| | 11.55863 | 9.98438 | |
| Average | 11.55863 | 9.98428 | 0.86127 |

| Weight of $LaBr_3$ in vacuum, g. | Weight of toluene displaced in vacuum, g. | Density of $LaBr_3$ 25°/4° |
|---|---|---|
| 2.3703 | 0.4036 | 5.058 |
| 2.1244 | 0.3619 | 5.056 |
| | | Average 5.057 |

| Weight of $LaCl_3$ in vacuum, g. | Weight of toluene in vacuum, g. | Density of $LaCl_3$ |
|---|---|---|
| 1.6061 | 0.3600 | 3.843 |
| 1.5146 | 0.3396 | 3.841 |
| | | Average 3.842 |

Earlier determinations of the density of lanthanum chloride are:

| | | |
|---|---|---|
| Matignon,[17] displacement of nitrobenzene | 18°/4° | 3.947 |
| Bourion,[18] displacement of amyl benzoate | 0°/4° | 3.79 |
| Kleinheksel and Kremers,[19] displacement of air | 25°/4° | 3.82 |

## III. THE INCREASED EFFICIENCY OF CALCIUM BROMIDE AS A DRYING AGENT AT LOW TEMPERATURES

In the preceding investigation on the atomic weight of lanthanum a current of dry hydrogen bromide was necessary. This gas reacts with concentrated sulfuric acid and with phosphorus pentoxide[20] and therefore has frequently been dried by fused calcium bromide. This substance, though rapid in its effect, leaves 0.2 mg. of moisture in air passed over it.[21] We therefore adopted the expedient of chilling the calcium bromide with carbon dioxide snow and alcohol. Although the temperature was thus lowered to the neighborhood of the boiling point of the hydrogen bromide, no condensation actually took place, owing doubtless in part to the fact that the hydrogen bromide was diluted with a small percentage of hydrogen.

In order to determine the efficiency of this method we carried out the following experiments. Pure calcium bromide was freshly fused and

[17] Matignon, *Compt. rend.*, **140,** 1339 (1905).

[18] Bourion, *Ann. chim. phys.*, **21,** 65 (1910).

[19] Kleinheksel and Kremers, THIS JOURNAL, **50,** 963 (1928).

[20] Bailey and Fowler, *Chem. News*, **58,** 22 (1888); Baxter and Hines, THIS JOURNAL, **28,** 779 (1906).

[21] Baxter and Warren, *ibid.*, **33,** 340 (1911).

packed in a U-tube. Into one side could be passed pure air of low humidity. The other side could be connected with a counterpoised U-tube containing phosphorus pentoxide.

A measured volume of air was first aspirated at the rate of two liters per hour through the system with the calcium bromide at 25° (Experiments 1 and 2). The results confirmed those of Baxter and Warren. The experiments were then repeated with the calcium bromide at −72° (Experiments 3 and 4). The calcium bromide was then removed from the U-tube and the experiments repeated (Experiments 5 and 6). In these experiments a mist condensed in the chilled U-tube. Since in Experiments 5 and 6 the removal of the water from the air seemed to be as complete without the calcium bromide as when it was used, and since in none of the Experiments 3 to 6 was the water obtained much greater than the experimental uncertainty, further experiments were then made, with (Experiments 7 to 9) and without (Experiments 10 and 11) the use of calcium bromide at −21° (salt and ice). In these a real increase in efficiency appeared if the calcium bromide was used. The following table gives the experimental data.

| Experiment | Temp., °C. | Tube | Volume of air S. T. P., liters | Weight of water, mg. | Weight of water per liter, mg. |
|---|---|---|---|---|---|
| 1 | 25 | $CaBr_2$ | 7.3 | 1.2 | 0.16 |
| 2 | | | 7.2 | 0.8 | .11 |
| | | | | | Average .14 |
| 3 | −72 | $CaBr_2$ | 14.5 | .20 | .014 |
| 4 | | | 14.5 | .15 | .010 |
| | | | | | Average .012 |
| 5 | | Empty | 14.5 | .20 | .014 |
| 6 | | | 14.5 | .25 | .017 |
| | | | | | Average .016 |
| 7 | −21 | $CaBr_2$ | 14.6 | .30 | .020 |
| 8 | | | 14.5 | .25 | .017 |
| 9 | | | 14.6 | .30 | .020 |
| | | | | | Average .019 |
| 10 | | Empty | 14.5 | .70 | .048 |
| 11 | | | 14.5 | .60 | .041 |
| | | | | | Average .045 |

These experiments are of interest in establishing both that calcium bromide is considerably more efficient at low temperatures and that the speed with which it removes residual water from a gas current is sufficiently high. Presumably the efficiency of other drying agents may be similarly increased.

## Summary

1. The preparation of anhydrous lanthanum bromide is described.

2. The analysis of this salt by comparison with silver and by weighing the resulting silver bromide is found to yield 138.92 as the atomic weight of lanthanum.

3. The specific gravities of anhydrous lanthanum chloride and bromide at 25° are found by displacement of toluene to be 3.842 and 5.057, respectively.

4. The greater efficiency of calcium bromide as a drying agent at low temperatures is experimentally investigated.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# ADSORPTION AND REACTIONS AT SURFACES OF ZINC OXIDE

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The present investigations originated in an attempt to obtain additional experimental data on the decomposition of alcohols at oxide surfaces in order to test two alternative theories for the distribution of decomposition between dehydrogenation and dehydration reactions at such surfaces. The two theories may be described as the Adkins–Burk–Balandin theory of multiple attachment at surfaces having varied spacings which determine the mode of decomposition and the Taylor theory of dual surfaces according to which the mode of decomposition is determined by the ionic charge of the group to which the adsorbed alcohol molecule is attached. There is no necessity to set forth the evidence for and relative merits of the two points of view since this has recently been independently done in detail by Schwab[1] in his recent text on catalysis. It will suffice to summarize the experiments performed with respect to the alternative reactions at various surfaces of zinc compounds, to emphasize the limited nature of the conclusions which may, as yet, be safely drawn from such work, and finally to detail the results concerning the adsorption of water vapor and hydrogen at zinc oxide surfaces, indicating their paramount importance in this problem of alternative reactions at a given surface.

Prior to the adsorption experiments a very large number of experiments were made with the object of obtaining definitive data on the velocity, nature and temperature coefficients of the decomposition of isopropanol on various zinc compound surfaces. As the result of a mass of experimental data obtained over a period of one year with six different types of surface, we are forced to the conclusion that *much of what has previously been deduced as characteristic of such surfaces is based on an entirely too restricted range of experimental measurements.* Our multiplication of such measurements served to show definitely that for even *approximately* reproducible results the most stringent regulation of a variety of experimental details must be arranged. Similar apparently capricious results

[1] Schwab, "Katalyse vom Standpunkt der chemischen Kinetik," Julius Springer, Berlin, 1931, pp. 173, 184–186, 203.

were obtained by Smith and Hawks[2] in their studies of methanol decomposition at zinc and cadmium oxide surfaces.

In our experimental arrangement the most careful attention was given to precision of experimental details. The alcohol was passed at carefully controlled speeds over small (1–2 g.) samples of the compound under study which was heated in an automatically controlled fused salt-bath maintained at temperatures varying not more than $\pm 0.1°$ during an experiment. In addition, a thermocouple embedded within the solid gave us an indication of the temperature obtaining within the mass. It is significant that this latter was frequently 50° lower than the bath temperature so that the mass could, therefore, not be at a uniform temperature throughout. The alcohol was specially prepared by hydrogenation of acetone at a nickel surface, any acetone removed by shaking with sodium bisulfite, the product being dried carefully with lime. It was free of acetone and contained less than 0.1% of water. Six different types of zinc compound were prepared under carefully controlled conditions and utilized for these studies: zinc oxide I, *ex* oxalate, by ignition in a current of air at 400° of pure zinc oxalate (*ex* zinc nitrate and ammonium oxalate molar solutions); zinc oxide II, a commercial C. P. product; zinc oxide III, made by adding excess sodium hydroxide to a hot solution of C. P. zinc sulfate, washing until free of sulfates and drying at 250°; zinc oxide IV, a second sample prepared as in the case of III except that all washing was omitted.[3] Normal zinc phosphate, V, was made from C. P. zinc oxide and U. S. P. phosphoric acid, following the directions of Eberly, Gross and Crowell.[4] Zinc pyrophosphate, VI, was made by heating zinc ammonium phosphate to 400° in a current of air.

In view of the capricious behavior exhibited in all of this work on reactions we have decided to abstain from the presentation of any experimental results and to content ourselves with formulating the only conclusions that may with certainty be drawn from the whole body of experimental data. These conclusions may thus be summarized.

(1) The decomposition of isopropanol at zinc oxide surfaces is not zero order at atmospheric pressure. Thus, on zinc oxide I at a temperature of $341 \pm 3°$ an increase in rate of alcohol passage from 25 to 80 cc. liquid alcohol per hour resulted in a corresponding steady increase in gas yield from 57.7 cc. per minute at the lower to 94 cc. per minute at the upper rate of alcohol flow.

[2] Smith and Hawks, *J. Phys. Chem.*, **32**, 415 (1928).

[3] The two preparations III and IV were prepared with the object of duplicating a preparation of Lazier and Adkins, THIS JOURNAL, **47**, 1719 (1925), which appeared to possess predominantly dehydrating characteristics. Our lack of success in producing such a zinc oxide is discussed later.

[4] Eberly, Gross and Crowell, *ibid.*, **42**, 1433 (1920).

(2) The dehydrogenation–dehydration ratio is not characteristic for particular methods of preparation so far as these can at present be defined nor does it vary with temperature in the same way for different preparations. Thus, on zinc oxide I the apparent activation energies of dehydrogenation and dehydration were, respectively, about 14 and 20 kg. cal. On zinc oxide II the activation energy of dehydrogenation was 30 kg. cal. On zinc oxide III, a more active surface than zinc oxide I, both the dehydrogenation and dehydration reactions have energies of activation of approximately 20 kg. cal.

(3) Zinc oxide, whatever the source, is predominantly dehydrogenating ($> 90\%$). Large quantities of salts (as in zinc oxide IV) reduce the activity but do not destroy it. Zinc oxide IV gave 63.7 cc. of gas per minute at 372°, whereas zinc oxide III gave this rate at approximately 290° when the alcohol flow was 50 cc. per hour. The gas in each case was $> 98\%$ hydrogen. We are at a loss to explain the result of Lazier and Adkins[3] already cited unless their abnormal dehydration values are to be attributed to the presence of tertiary alcohols in their reaction material.

(4) Zinc ortho- and pyrophosphate are almost exclusively dehydrating catalysts. This observation points definitely to the importance of the 3- and 4-valent anions in determining dehydration.

(5) Water is a strong reversible poison for zinc oxide catalysts. The presence of 1% of water in the isopropanol decreased the rate of decomposition to one-half the value with anhydrous alcohol. Our experimental evidence indicated that water produced by the dehydration process was even more pronouncedly retarding than the added water. It was this observation which led to the following investigation of the adsorption of water by zinc oxide I in an effort to obtain independent evidence of the importance of adsorbed water in the decomposition process.

## I. The Adsorption of Water Vapor by Zinc Oxide I

**Apparatus and Method.**—The apparatus consisted of a bulb containing the catalyst connected to a constant volume manometer and through stopcocks to a mercury pump evacuation system and a 100-cc. bulb which was connected through a three-way stopcock to a mercury reservoir and a small bulb containing water. The catalyst tube was heated to a constant temperature by an electric furnace. This furnace consisted of a Pyrex Dewar flask wrapped on the outside with a heating coil of nichrome wire. A capillary tube connected the annular space between the walls of the Dewar flask with a U-tube provided with sealed-in platinum contacts and containing mercury. A relay connected through these mercury contacts regulated the current heating the Dewar flask, the expansion or contraction of the air in the annular space in the Dewar flask operating the relay. The bulb containing the catalyst was placed inside the Dewar flask. The temperature of the catalyst could be kept constant within 0.1°.

Pure zinc oxalate was placed in the catalyst bulb and gradually heated to 400° with the pumps running. When gas evolution had apparently ceased, the temperature was raised to 450° and the catalyst evacuated at this temperature for ten hours. The catalyst was cooled to room temperature, and water vapor added to the system by

opening the 100-cc. bulb to the small bulb of water, which was immersed in ice or water at a temperature below that of the room, closing off from the water after ten minutes, opening the 100-cc. bulb to the catalyst and finally filling the bulb with mercury to drive all the water vapor into the catalyst system. These operations were repeated until the desired amount of water had been admitted. The catalyst was then heated to the temperature at which the vapor pressure of the adsorbed water was to be measured, and maintained at that temperature until the pressure remained constant. It was then heated to a higher temperature, the pressure noted, etc. The results were checked by making a similar series of determinations at decreasing temperatures.

## Experimental Results

Preliminary measurements indicated a large adsorption even at high temperatures, much larger than was expected. The results of more precise measurements are given in Table I.

TABLE I

ADSORPTION OF WATER VAPOR ON 10 G. OF ZINC OXIDE I

Total water vapor in system, cc. N. T. P.

| 10.45 | | | 11.34 | | | 12.56 | | |
|---|---|---|---|---|---|---|---|---|
| $T$, °C. | $P_{mm.}$ | $V_{ads.,cc.}$ | $T$, °C. | $P_{mm.}$ | $V_{ads.,cc.}$ | $T$, °C. | $P_{mm.}$ | $V_{ads.,cc.}$ |
| 313 | 1.4 | 10.38 | 298 | 1.3 | 11.27 | 298 | 2.5 | 12.43 |
| 318 | 1.9 | 10.35 | 315 | 2.3 | 11.22 | 315 | 4.4 | 12.34 |
| 330 | 2.8 | 10.31 | 333 | 4.5 | 11.12 | 333 | 7.7 | 12.17 |
| 340 | 3.8 | 10.26 | 352 | 8.2 | 10.92 | 352 | 13.5 | 11.88 |
| 352 | 5.9 | 10.15 | 372 | 15.6 | 10.57 | 372 | 24.1 | 11.36 |
| 372 | 10.3 | 9.93 | 386 | 22.9 | 10.34 | | | |
| 386 | 15.9 | 9.65 | | | | | | |
| 401 | 21.4 | 9.39 | | | | | | |

A plot of the logarithm of the pressure as a function of the reciprocal of the absolute temperature gave straight lines, from which adsorption isosteres were constructed. The heat of adsorption, given in Table II, was calculated by means of the Clapeyron equation.

TABLE II

HEAT OF ADSORPTION OF WATER ON ZINC OXIDE I

| | | |
|---|---|---|
| Amount adsorbed, cc. N. T. P. per gram | 1.03 | 1.12 |
| Heat of adsorption, calories | 30,300 | 32,200 |

The catalyst adsorbed water vapor almost instantly at room temperatures. Attempts to detect the "activated" adsorption shown by Taylor[5] to occur on adsorption of hydrogen, oxygen and carbon monoxide by active catalysts were made. It was expected that if a catalyst which had adsorbed water vapor at room temperature, presumably in the unactivated form, as indicated by the rapid adsorption at this temperature, were rapidly heated, the water vapor would desorb and then return to the surface at a higher temperature. The expected rise and subsequent fall of pressure on heating was not observed in any of a number of experiments. However,

[5] H. S. Taylor, THIS JOURNAL, **53**, 578 (1931).

evidence that there is a second type of adsorption of water requiring an activation energy was obtained by adding water vapor to the catalyst, not at room temperature, but at 250–270°. The first portions of water vapor admitted were again adsorbed very rapidly, but after considerable water had accumulated on the surface the adsorption became measurably slow. Lack of time prevented a thorough investigation, but the results obtained show conclusively that at high temperatures a slow adsorption appears. The data presented in Table III indicate the type of results obtained.

TABLE III

RATE OF ADSORPTION OF WATER BY 10 G. OF ZINC OXIDE I

14.7 cc. N. T. P. $H_2O$ already on surface; 2.09 cc. N. T. P. $H_2O$ added. Total $H_2O$ in system, 16.8 cc. N. T. P.

| Time after adding water, minutes | Pressure mm. | Temperature, °C. |
|---|---|---|
| 10 | 5.5 | 248 |
| 22 | 3.5 | 249 |
| 30 | 2.9 | 249 |
| 55 | 2.0 | 250 |
| Temperature raised to 270° | 2.4 | 270 |

A second addition of 2.09 cc. N. T. P. of water was made. Total $H_2O$ in system, 18.9 cc.

| | | |
|---|---|---|
| 0 | 17.8 | 270 |
| 5 | 14.5 | 270 |
| 10 | 13.7 | 270 |
| 20 | 13.0 | 270 |
| 30 | 12.8 | 270 |
| 50 | 12.2 | 270 |
| 200 | 11.5 | 270 |
| 260 | 11.3 | 270 |

On lowering the temperature to 25°, the pressure became 0.0 mm.

## Discussion

With a fresh catalyst, desorption was very slow, ten hours or more being required to reach equilibrium at high temperatures. After water had been adsorbed and removed by evacuation at 450°, this slow attainment of equilibrium was much less apparent, and slightly higher vapor pressures were obtained. As the catalyst had already been heated to this temperature, and as evidence presented in the section on the adsorption of hydrogen proves that the catalyst does not progressively sinter at 450° in a high vacuum, it is likely that the last traces of water are not removed by the evacuation process, and the figures given for the amount adsorbed are probably somewhat too low.

The amount of water adsorbed is remarkable, and is much larger than that of hydrogen (see Part II), and the heat of adsorption is higher. In the absence of other data this would indicate that zinc oxide I should be

at least as good a dehydration catalyst as a dehydrogenation catalyst.[6] As the water formed by the dehydration process must, however, escape from the surface if the process is to continue, the energy necessary to remove the water from the surface must be considered.

That this may be the dominating factor in determining the rate of dehydration is rendered probable when we consider that, as pointed out by Taylor,[5] the activation energy of desorption is the sum of the heat of adsorption and the activation energy of the water adsorption. We have seen that the heat of adsorption is *ca.* 30,000 calories; the activation energy of the water adsorption is probably not less than 15,000–20,000 calories, considering the temperature (250–270°) at which slow adsorption is manifested, giving an activation energy of evaporation of the adsorbed water of at least 45,000 calories on a large part of the surface having dehydrating ability. This accounts for the marked poisoning of water on the dehydration process.

The desorption of the water will be aided by decreasing the partial pressure of water in the gas in the neighborhood of the catalyst surface. This was actually observed in the decomposition experiments, for a relative increase in the dehydration reaction was observed with increasing rates of alcohol flow.

## II. The Adsorption of Hydrogen by Zinc Oxide I

The adsorption of hydrogen on zinc oxide has been studied by Lazier and Adkins,[7] who found that at 22° and 740 mm. a 100-g. sample of zinc oxide *ex* hydroxide adsorbed 1.8 cc. at N. T. P. of hydrogen, and that 100 g. of zinc oxide *ex* isopropoxide adsorbed 23.4 cc. at N. T. P.; and by Taylor and Kistiakowsky,[8] who measured a number of isotherms on zinc oxide I. Garner and Kingman[9] have recently studied a zinc oxide preparation with a very minute adsorption for hydrogen.

Recent advances in the theory of activated adsorption[10] have made further study of zinc oxide desirable.

### Theoretical

The theory and importance of adsorption requiring activation energy is given in the last three papers quoted above.[10] As experimental material illustrating some of the points will be presented, it is desirable to indicate the simplest form of the theory of the now characteristic adsorption isobars of adsorption on active catalysts.

[6] Pease, THIS JOURNAL, **45**, 1196, 2235 (1923).

[7] Lazier and Adkins, *J. Phys. Chem.*, **30**, 353 (1926).

[8] Taylor and Kistiakowsky, THIS JOURNAL, **49**, 2468 (1927).

[9] Garner and Kingman, *Trans. Faraday Soc.*, **37**, 322 (1931).

[10] H. S. Taylor, THIS JOURNAL, **53**, 578 (1931); Taylor and Williamson, *ibid.*, **53**, 2168 (1931); H. S. Taylor, *Chem. Reviews*, **9**, 1–46 (1931).

Suppose adsorption taking place at constant pressure on a plane uniform surface with an activation energy $E$ and a heat of adsorption $\lambda$, which are assumed constants independent of the amount adsorbed. The rate of condensation of gas molecules on the surface will be proportional to the number of molecules striking the surface per unit time with an energy greater than $E$, that is, roughly, the rate of condensation $= k_1 e^{-E/RT}$. The rate of evaporation will be proportional[5] to $e^{-(E+\lambda)/RT}$, and to the fraction of the surface covered or, roughly, the rate of evaporation $= k_2 v e^{-(E+\lambda)/RT}$, where $v$ is the volume adsorbed after the time $t$. The total rate of adsorption will be

$$\frac{dv}{dt} = k_1 e^{-(E/RT)} - k_2 v e^{-(E+\lambda)/RT} \quad (1)$$

When equilibrium prevails, $dv/dt = 0$, and

$$v_0 = \frac{k_1}{k_2} e^{\lambda/RT} \quad (2)$$

where $v_0$ is the quantity adsorbed at equilibrium at the given pressure.

Integrated, equation (1) gives, using the boundary condition that $v = 0$ when $t = 0$

$$v = \frac{k_1}{k_2} e^{\lambda/RT}\left(1 - e^{-k_2 t e^{-(E+\lambda)/RT}}\right) = v_0\left(1 - e^{-k_2 t e^{-(E+\lambda)/RT}}\right) \quad (3)$$

Equation (3) may be put in the more convenient logarithmic form

$$\log_e (v_0 - v) = \log_e v_0 - k_2 t e^{-(E+\lambda)/RT} \quad (4)$$

Thus the graph of $\log_e (v_0 - v)$ as a function of $t$ is a straight line whose slope is $-k_2 e^{-(E+\lambda)/RT}$. This affords a convenient graphical method of determining $v_0$ by assuming values for $v_0$ and plotting $\log_e (v_0 - v)$ as a function of $t$ until a satisfactory straight line is obtained. If $k_2$ is known[5] $E + \lambda$ may be calculated, or conversely if $E$ and $\lambda$ are known, $k_2$ may be calculated. By plotting the logarithm of the negative of the slope of equation (4) as a function of $1/T$ a straight line should again be obtained whose slope obviously allows $E + \lambda$ to be calculated independently of any assumption of the order of magnitude of $k_2$.

The isobaric adsorption given by equation (3) has one extremum whose position $T_{max.}$ is obtained by solving $dv/dT = 0$ for $T$. This extremum proves to be a maximum for even very improbable values of $k_1$, $k_2$, $E$ and $\lambda$. Essentially, we are led to solve the equation

$$1 + \frac{k_2 t (E+\lambda)}{\lambda} e^{-(E+\lambda)/RT_{max.}} - e^{k_2 t e^{-(E+\lambda)/RT_{max.}}} = 0$$

or putting

$$k_2 t e^{-(E+\lambda)/RT} = z$$

the equation

$$1 + \frac{E+\lambda}{\lambda} z = e^z$$

This equation has a root different from 0, say $z_0$, best obtained graphi-

cally. The isobar will have a maximum if $z_0 < k_2 t$, the corresponding temperature $T_{max.}$ being

$$T_{max.} = \frac{E + \lambda}{R \log_e (k_2 t / z_0)} \qquad (5)$$

## Experimental

**Apparatus and Experimental Method.**—The apparatus and experimental method were those of Taylor and Williamson.[10] This apparatus consisted of a system of pumps, manometer, burets, etc., which allowed a quantity of pure dry hydrogen to be admitted to the evacuated catalyst, which was maintained at a constant temperature, and the rate of pressure change to be measured, from which the rate of adsorption could be calculated from the known volume of the system.

The catalysts were prepared from pure zinc oxalate as in Part I; 20.0-g. samples were used. The catalyst was pumped off in a high vacuum for three to four hours at 450° between runs.

**Experimental Results.**—The results of the velocity determinations are given graphically in Fig. 1 and one typical series of measurements, that for 184°, is given in Table IV.

TABLE IV

RATE OF ADSORPTION OF HYDROGEN BY 20 GRAMS OF ZINC OXIDE I AT 184°

| Time, mins. | Pressure, mm. | Amount adsorbed in cc., N. T. P. | Time, mins. | Pressure mm. | Amount adsorbed in cc., N. T. P. |
|---|---|---|---|---|---|
| 0 | | 0 | 75 | 423.5 | 8.10 |
| 2 | 539.5 | 2.25 | 90 | 417.5 | 8.40 |
| 5 | 505.5 | 3.95 | 105 | 412.0 | 8.70 |
| 10 | 486.0 | 4.90 | 120 | 407.5 | 8.95 |
| 15 | 474.0 | 5.60 | 135 | 402.5 | 9.20 |
| 20 | 467.0 | 5.90 | 160 | 396.0 | 9.50 |
| 25 | 459.5 | 6.30 | 180 | 392.0 | 9.70 |
| 30 | 454.0 | 6.55 | 210 | 387.0 | 9.95 |
| 35 | 449.0 | 6.80 | 230 | 384.0 | 10.10 |
| 40 | 444.5 | 7.05 | 360 | 363.0 | 11.15 |
| 45 | 440.5 | 7.25 | 420 | 355.5 | 11.50 |
| 50 | 437.5 | 7.40 | 510 | 345.5 | 12.05 |
| 55 | 434.5 | 7.55 | 1165 | 315.0 | 14.10 |
| 60 | 431.5 | 7.70 | | | |

The experiments were made in the order, 0, 110, 132, 184, 218 and 306°. The heats of activation calculated from these data are given in Table V, which shows the reliability limits of the velocity measurements.

After obtaining these rates an attempt was made to measure isotherms at 306 and 444°. Progressively diminishing values for the amount of adsorption in successive runs and darkening of the catalyst vitiated the results. Nevertheless, a heat of adsorption of *ca.* 16,000 calories was indicated on the now ruined catalyst. The total adsorption fell to about

TABLE V

ACTIVATION ENERGY OF HYDROGEN ADSORPTION BY ZINC OXIDE I

| Amount adsorbed cc. N. T. P. | Activation energy, Kg. calories 110–132° | 132–184° | 184–218° | 218–306° |
|---|---|---|---|---|
| 3.0 | 7.6 | 7.0 | 3.8 | .. |
| 3.5 | 9.0 | 7.5 | 8.0 | .. |
| 4.0 | 13.2 | 9.5 | 10.5 | .. |
| 4.5 | 14.4 | 11.4 | 10.7 | .. |
| 5.0 | 15.4 | 12.7 | 10.5 | .. |
| 5.5 | 16.0 | 13.4 | 10.0 | 12.1 |
| 6.0 | 15.9 | 14.0 | 10.3 | .. |
| 6.5 | .. | 14.4 | 10.3 | .. |
| 7.0 | .. | 14.4 | 10.9 | .. |
| 7.5 | .. | 14.7 | 11.0 | .. |
| 8.0 | .. | .. | 11.2 | .. |
| 8.5 | .. | .. | 11.1 | .. |
| 9.0 | .. | .. | 11.1 | .. |

one-third of its initial value, certainly due to destruction of active areas by reduction.[11]

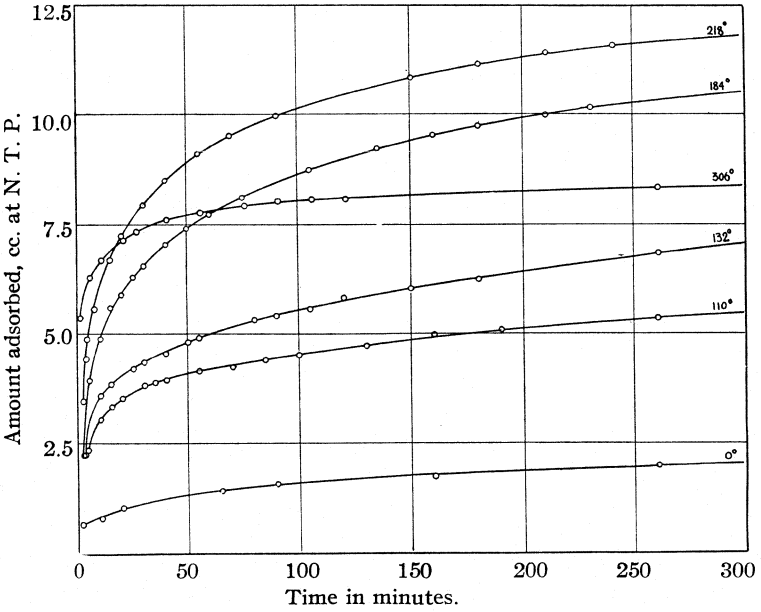


Fig. 1.—Rate of adsorption of hydrogen by 20.0 g. of zinc oxide I.

A velocity run at 184° with a fresh catalyst gave initially an abnormally high rate and adsorbed amount compared to the former catalyst. After this run, an attempt was made to recover the hydrogen by evacuation

[11] Taylor and Starkweather, THIS JOURNAL, **52**, 2314 (1930).

with a Sprengel pump. At 184° the dead space was quickly pumped out, but desorption occurred very slowly. By gradually raising the temperature to 450° and pumping overnight, the volume of hydrogen admitted was recovered quantitatively, showing that no reduction of the catalyst had taken place. A repetition of the velocity determination at 184° now gave results so nearly the same as those given in Fig. 1 that the catalysts may be considered as identical.

Isotherms in liquid air and solid carbon dioxide were next made with the results shown in Fig. 2, which also gives the final amount adsorbed and final pressures of the velocity runs of Fig. 1. From these data the isobaric adsorption at 400 mm. shown in Fig. 3 was calculated.

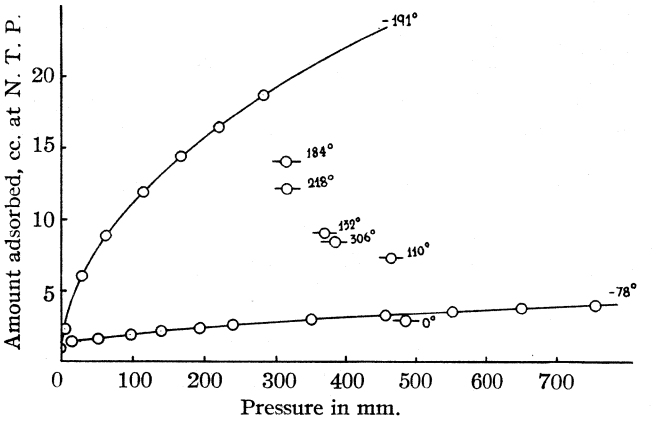


Fig. 2.—Adsorption isotherms of hydrogen on 20.0 g. of zinc oxide I.

## Discussion

The activation energy of the "activated" adsorption of hydrogen on zinc oxide I has already been given. The excellent internal agreement of these activation energies proves that the catalyst does not sinter progressively at 450° in high vacuum, and that three to four hours pumping at this temperature gave a reproducible surface. The latter part of the rate curves at 184 and 218° gave straight lines when fitted to equation (4) of the preceding theoretical discussion, which indicates that $E + \lambda$ is constant over the latter portions of the surface covered by the hydrogen. From the equation so obtained values for $v_0$ at 184 and 218° were calculated. From these and equation (2) a value of 20,800 calories was calculated for the heat of adsorption, a better value than the 16,000 calories obtained from the "isotherms" on the partially deactivated catalyst. Using a value of $E = 14{,}000$ calories and $\lambda = 21{,}000$ calories, a value of $k_2 = 9.25 \times 10^{12}$ was calculated from equation (4). $k_1/k_2$, and, if desired, $k_1$ can be calculated from the data already obtained and equation (2).

Thus $z_0$ was found to be 0.947, and from equation (5) a value of $T_{max.} = 470°A.$ was calculated for a time $t = 1200$ minutes, approximately the time used in constructing Fig. 3, which shows the temperature of the maximum adsorption to be $T_{max.} = 450°A.$, a much better agreement than might be expected.

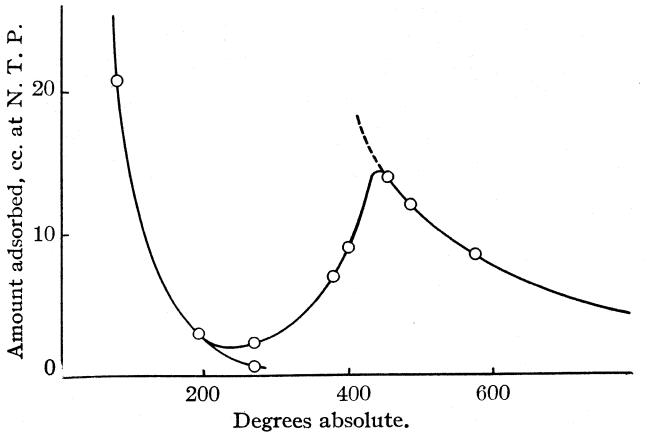


Fig. 3.—Adsorption isobar of hydrogen on 20.0 g. of zinc oxide I at 400 mm. pressure.

As on the manganese catalysts studied by Taylor and Williamson,[10] the activation energy for the first portions of gas adsorbed is much lower than the more or less constant value obtained for the less active spots. Attention should also be called to the fact that equilibrium was obtained in less than one minute at liquid air and solid carbon dioxide temperatures, indicating a negligible activation energy for the low temperature adsorption process.

From the low temperature isotherms given in Fig. 3 a heat of adsorption for the low temperature process of 1100 calories was calculated from the Clapeyron equation. This should be compared with the 21,000 calories of the activated adsorption.

Thus the two types of adsorption to be expected on active catalysts have again been demonstrated, one form occurring rapidly at low temperatures with a low heat of adsorption, the other occurring at much higher temperatures with a very much higher heat of adsorption and with a rate increasing exponentially with temperature. At intermediate temperatures these two forms may overlap.

## Summary

1. The difficulties attending measurements of the velocity of decomposition of alcohols on zinc oxide surfaces have been indicated.

2. The adsorption of water vapor by such surfaces is an important factor in the velocity of decomposition of alcohols.

3. The vapor pressure of water adsorbed on zinc oxide *ex* oxalate has been measured at 300–400°.

4. The heat of adsorption of water vapor, probably of the activated form, on zinc oxide *ex* oxalate is approximately 30,000 calories.

5. Evidence for the activated adsorption of water on zinc oxide *ex* oxalate has been obtained.

6. An explanation of the low dehydration–dehydrogenation ratio of zinc oxide has been given.

7. The velocity of the adsorption of hydrogen by zinc oxide *ex* oxalate has been measured in the temperature interval 0–306°, and isotherms have been obtained at −191 and −78.5°.

8. Two types of adsorption of hydrogen by zinc oxide *ex* oxalate have been distinguished, their heats of adsorption determined, and the activation energy for the activated type has been measured over a wide range.

9. The theory of activated adsorption has been developed mathematically, leading to expressions for the temperature of maximum adsorption, and methods of calculating the activation energy and heat of adsorption in difficult cases have been presented.

10. Except in the initial stages, the theoretical equations reproduce the course of the activated adsorption of hydrogen on zinc oxide with great fidelity.

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[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, ALABAMA POLYTECHNIC INSTITUTE]

## FURTHER RESEARCH ON ELEMENT 87

BY FRED ALLISON, EDNA R. BISHOP, ANNA L. SOMMER AND J. H. CHRISTENSEN

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Detection of element 87 in pollucite and lepidolite was announced by Allison and Murphy.[1] They employed the magneto-optic method[2] which was developed in this Laboratory.

In continuing this research, a more extended study was made to determine whether the minima attributed to compounds of 87 might be due to some other substance and a search was made for other sources of 87.

In this work, water solutions of the substances studied were prepared. Soluble salts were simply dissolved; insoluble ones were extracted with acid or aqua regia. The desired anion was obtained by adding the appropriate acid or sodium hydroxide and the solution was then examined by the magneto-optic method. Every substance was examined both as

[1] Allison and Murphy, *Phys. Rev.*, **35**, 285 (1930).

[2] Allison, *ibid.*, **30**, 66 (1927); Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

the chloride and sulfate; some also as the nitrate and hydroxide. Readings were made visually and the more important ones were checked with a photo-electric cell.

The characteristic minima attributed to 87 are located on our scale as shown in Table I.

TABLE I

SCALE READINGS OF COMPOUNDS OF ELEMENT 87

| 87Cl | $87NO_3$ | $87_2SO_4$ | 87OH |
|---|---|---|---|
| 44.01 | 11.48 | 30.48 | 22.08 |
| 44.62 | 11.66 | 30.85 | 22.40 |
| 45.11 | 11.98 | 31.35 | 22.82 |
| 46.22 | 12.28 | 32.02 | 23.18 |
| 46.42 | 12.67 | 32.32 | 23.66 |
| 47.80 | 12.94 | 32.71 | 24.06 |

Examination of the table of scale readings of other elements[2] shows that these minima must be produced by the compounds of a cation whose equivalent weight is greater than $Tl^+$. This limits us to element 87 and complex ions.

Ammonia complex ions are eliminated at once as they do not exist in acid solution. $SnCl_3^+$ and $ReCl^+$ have been suggested.[3] To test these possibilities, nitric acid solutions of pollucite and lepidolite, free from chloride, were prepared. The minima of 87 nitrate were present. Sulfuric acid was added and the minima of 87 sulfate were obtained. Therefore, the minima attributed to 87 cannot be due to any complex chloride.

To prove this point further, a careful examination of stannic chloride solutions was made and showed not only the regular eleven minima at 19.94, 20.02, 20.06, 20.15, 20.23, 20.28, 20.34, 20.40, 20.45, 20.51 and 20.55 but also four minima at 44.18, 44.40, 44.98 and 46.06. It will be seen that these do not coincide with any of the six 87 chloride minima and can be accurately distinguished from them. Furthermore, these four minima disappear after reduction with sulfur dioxide or conversion into the stannate by the addition of excess sodium hydroxide, whereas 87 chloride minima persist after each of these treatments.

Similarly rhenous chloride solutions were examined. In addition to the regular minima at 32.55 and 32.65, two were found, one at 45.93 and one at 47.54. These were not destroyed by the addition of nitric acid but did disappear on the addition of perchloric acid, whereas 87 minima persisted after the addition of an excess of perchloric acid.

Since we have found nothing else which might give the minima attributed to compounds of 87 and since these minima persist after treatment with acids, bases, oxidizing and reducing agents, we conclude, as previously announced, that these minima are due to element 87.

[3] Papish and Wainer, THIS JOURNAL, **53**, 3818 (1931).

The six minima indicate the probable existence of six isotopes.[4] The long distance covered on the scale suggests considerable difference in weight, possibly transition products in a radioactive transformation.

In addition to pollucite and lepidolite, previously reported, we have found element 87 in sea water, Searles Lake (California) brine, kainite (Stassfurt), crude cesium chloride, monazite sand (Brazilian and North Carolinian) and samarskite[5] (Brazilian, Norwegian and several American samples).

Although the tin and rhenium minima were usually present in samples that contained 87, they were easily distinguished from each other on the scale; they occur in different relative amounts as shown in Table II; furthermore, the tin and rhenium minima were destroyed by the chemical treatment indicated above while 87 minima persisted.

TABLE II

APPROXIMATE CONCENTRATION IN GRAMS OF SAMPLE PER CUBIC CENTIMETER OF SOLUTION AT WHICH MINIMA FROM 44 TO 48 ON THE SCALE APPEAR

The scale readings of these minima are not such as could be attributed to the chlorides of $Sn^{++++}$ and $Re^{++}$. Moreover, the minima due to the chlorides of $Sn^{++++}$ and $Re^{++}$ persist on dilution after the above minima have disappeared.

| Sample | $SnCl_4$ | $ReCl_2$ | 87Cl |
|---|---|---|---|
| Crude cesium chloride (prepared from pollucite) | $2/10^5$ | $2/10^4$ | $2/10^4$ |
| Monazite (Brazilian) | $2/10^5$ | $2/10^4$ | $2/10^2$ |
| Kainite (Stassfurt) | [not present at $2/10^2$] | $2/10^3$ | $2/10^2$ |
| Samarskite (Brazilian) | $2/10^5$ | $2/10^4$ | $2/10^3$ |
| Samarskite (N. C.) | $2/10^5$ | $2/10^4$ | $2/10^4$ |

Since the apparatus detects a few parts in $10^{12}$, the above samples would contain approximately one part in $10^8$, $10^{10}$, $10^{10}$, $10^9$ and $10^8$, respectively, of element 87. The concentration of this element in all substances examined is very low, ranging from a few parts in $10^{12}$ to $10^8$.

We suggest the name virginium and the symbol Va for element 87.

## Summary

Characteristic minima, as previously announced, have been obtained for the chloride, nitrate, sulfate and hydroxide of a cation whose equivalent weight is greater than $Tl^+$. It has been shown that these minima cannot be due to $SnCl_3^+$ or $ReCl^+$. They are attributed to element 87.

The characteristic minima of element 87 are not affected by acids, bases, oxidizing or reducing agents.

Element 87 appears to have six isotopes.

Several sources of element 87 were found but the concentration in each is very low.

AUBURN, ALABAMA

[4] Allison and Murphy, *Phys. Rev.*, **36**, 1097 (1930); Allison, *Ind. Eng. Chem.*, in press.

[5] The detection of 87 in samarskite by x-ray spectra has been reported by Papish and Wainer.[3]

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, ALABAMA POLYTECHNIC INSTITUTE]

# CONCENTRATION, ACIDS AND LITHIUM SALTS OF ELEMENT 85

BY FRED ALLISON, EDNA R. BISHOP AND ANNA L. SOMMER

RECEIVED NOVEMBER 25, 1931 PUBLISHED FEBRUARY 5, 1932

Evidence of the detection of element 85 by means of the magneto-optic method[1] was announced from this Laboratory.[2] Since that time, concentrations have been made and the studies of the oxidation and reduction reactions greatly extended to include the compounds formed. We suggest the name Alabamine and symbol Am for element 85.

**Concentration.**—The amount of alabamine was very small in all substances examined. Monazite sand (Brazilian) was chosen for the concentration work because of its availability and the ease with which the other substances present can be eliminated. Preliminary experiments which were checked by the magneto-optic method determined the method of procedure.

One hundred pounds of monazite were finely ground in a ball mill, digested with aqua regia and evaporated to dryness on a steam-bath. This was then extracted with water three times; appropriate minima showed that alabamine went into solution as peralabamic acid, $HAmO_4$. The solution was evaporated on a steam-bath and the remaining aqua regia displaced by sulfuric acid. When the volume was reduced to 800 cc., it was saturated with sulfur dioxide, which reduced the peralabamic acid to hydroalabamic acid, HAm; this was shown by the disappearance of minima of the former and the appearance of minima of the latter. The solution was made alkaline with lithium hydroxide, which precipitated out most of the heavy metals present. The filtrate was evaporated to 150 cc. and 600 cc. of alcohol was added to precipitate the lithium sulfate. The solution was filtered; the precipitate was washed with alcohol and the filtrate which contained the lithium alabamide was evaporated to 85 cc. Tests with the magneto-optic method showed that this solution contained approximately $2.5 \times 10^{-6}$ g. of alabamine as lithium alabamide, which represents a concentration of about 160 times.

**Acids and Lithium Salts of Element 85.**—In order to know where to expect minima for the oxygen compounds of alabamine and to identify what compounds are formed, minima were located for the corresponding hydrogen and lithium compounds of the other halogens. The results are shown in Tables I and II and are represented graphically in Fig. 1 by plotting scale readings against equivalent weights of the anion. These curves include many other oxygen acids and lithium salts in addition to those of the halogens. To change scale readings of the tables and curves

[1] Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

[2] Allison, Murphy, Bishop and Sommer, *Phys. Rev.*, **37**, 1178 (1931).

TABLE I

SCALE READINGS OF HALOGEN ACIDS

| | HX | HXO | $HXO_2$ | $HXO_4$ | $HXO_4$ | $H_5XO_6$ |
|---|---|---|---|---|---|---|
| | 15.75 | 8.25 | 4.75 | 2.46 | 1.86 | |
| Cl | 15.85 | 8.35 | 4.85 | 2.55 | 1.95 | |
| | 12.95 | 2.03 | 1.48 | 0.89 | 0.35 | |
| Br | 13.10 | 2.12 | 1.59 | 1.01 | 0.47 | |
| | 11.90 | 0.18 | −0.05 | −0.30 | −0.62 | 9.66 |
| I | 12.05 | 0.28 | +0.05 | −0.19 | −0.49 | 9.76 |
| | 10.98 | −1.64 | −1.94 | −2.28 | −2.60 | |
| Am | 11.10 | −1.55 | −1.83 | −2.17 | −2.50 | |

TABLE II

SCALE READINGS OF HALOGEN SALTS

| | LiX | LiXO | $LiXO_2$ | $LiXO_3$ | $LiXO_4$ | $Li_5XO_6$ |
|---|---|---|---|---|---|---|
| | 16.22 | 8.80 | 5.17 | 2.85 | 2.14 | |
| Cl | 16.45 | 8.95 | 5.28 | 2.95 | 2.28 | |
| | 13.40 | 2.27 | 1.82 | 1.10 | 0.68 | |
| Br | 13.60 | 2.38 | 1.93 | 1.20 | 0.78 | |
| | 12.37 | 0.42 | 0.23 | 0.03 | −0.36 | 10.05 |
| I | 12.58 | 0.51 | 0.33 | 0.14 | −0.26 | 10.16 |
| | 11.37 | −1.33 | −1.88 | −2.02 | −2.19 | |
| Am | 11.61 | −1.22 | −1.77 | −1.90 | −2.12 | |

to differential time lags[1] subtract 15 from the scale reading and multiply the difference by $10^{-9}$ second.

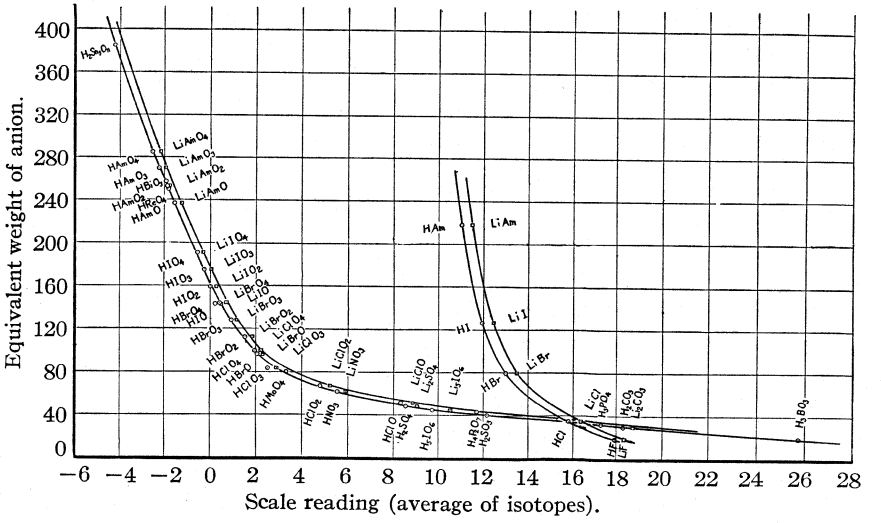


Fig. 1.—Scale readings of light minima as a function of equivalent weight of anion.

**Oxygen Compounds of Chlorine.**—Chlorine gas was passed into cold water and the minima for hypochlorous acid obtained. After stand-

ing for five days, these minima had disappeared and those of chlorous acid were present. Chloric acid minima were obtained from a solution made by passing chlorine through hot water and also checked with a potassium chlorate solution to which sulfuric acid had been added. Perchloric acid minima were read from a Merck commercial preparation.

Lithium hypochlorite, chlorite and chlorate were obtained by passing chlorine through a hot lithium hydroxide solution. Lithium perchlorate was prepared by adding an excess of lithium hydroxide to perchloric acid.

**Oxygen Compounds of Bromine.**—Bromine was added to water to give hypobromous acid and to lithium hydroxide to give lithium hypobromite. Bromous acid was prepared[3] by adding excess bromine water to silver nitrate solution, extracting the bromine with carbon disulfide and filtering. Lithium hydroxide was added to give lithium bromite. Bromic acid minima were obtained by adding sulfuric acid to potassium bromate.

Kämmerer[4] reported obtaining perbromic acid and chlorine gas by treating bromine with dilute perchloric acid. Other workers have generally failed to confirm his work.[5] The appearance of minima in the expected place substantiates his claim. The compound, however, is short lived. Perchloric acid was added to lithium hypobromite. The hypobromite and bromite minima disappeared. Bromate minima were present and two pairs appropriate to lithium perbromate and perbromic acid. These were gone after standing for twenty-four hours but were brought back by adding more perchloric acid. (These minima were not present in perchloric acid.) When the solution was made alkaline to litmus, the minima attributed to perbromic acid disappeared.

**Oxygen Compounds of Iodine.**—Iodine was added to water and two pairs of minima were obtained 0.18 and 0.28, −0.30 and −0.19. Potassium biiodate was dissolved in water and only the latter pair obtained, which were therefore attributed to iodic acid and the former to hypoiodic acid. On the addition of perchloric acid to the iodine in water solution, hypoiodous acid disappeared, iodic acid persisted and minima appropriate to $HIO_4$ and $H_5IO_6$ were obtained. (Other periodic acids were not looked for.) Work was interrupted for twenty days. The tube which contained undissolved iodine crystals had acquired a deep color and had to be diluted to let sufficient light through to make readings. $H_5IO_6$ minima were absent; $HIO_4$, $HIO_3$, HIO and two new minima at 0.05 and −0.05 which must be those of $HIO_2$ were present. Twenty-four hours later, only $HIO_2$ and HIO were present and both persisted for another twenty-four hours. Lithium hydroxide was added and lithium iodite minima were obtained.

[3] Richards, *J. Soc. Chem. Ind.*, **25**, 4 (1906).

[4] Kämmerer, *J. prakt. Chem.*, **90**, 190 (1863).

[5] Muir, *J. Chem. Soc.*, ii, 469 (1876); Wolfram, *Ann.*, **195**, 95 (1879); MacIvor, *Chem. News*, **33**, 35 (1876); **55**, 203 (1887); Robertson, *ibid.*, **106**, 50 (1912).

Iodine added to lithium hydroxide gave minima appropriate to lithium hypoiodite and lithium iodate. The latter was checked by adding lithium hydroxide to potassium biiodate. Perchloric acid was added to the iodine in lithium hydroxide solution, keeping it alkaline to litmus. Minima for LiIO, $LiIO_3$, $LiIO_4$ and $Li_5IO_6$ were obtained. After standing for twenty days this solution gave minima for $Li_5IO_6$ and $LiIO_4$ only.

**Oxygen Compounds of Alabamine.**—An iodine crystal was added to lithium alabamide solution which was neutral to litmus. The minima of lithium alabamide disappeared and those attributed to lithium hypoalabamite appeared. Later these disappeared and only those appropriate to lithium alabamite were present, while still later only those of lithium peralabamate were obtained.

When iodine was added to hydroalabamic acid, minima appropriate to all four oxygen acids were obtained. After standing, only peralabamic acid remained.

Bromine added to lithium alabamide gave minima of lithium hypoalabamite and alabamate immediately and only peralabamate after standing.

Perchloric acid was added to lithium alabamide in the presence of excess lithium hydroxide. Lithium hypoalabamite, alabamite and alabamate appeared at once and peralabamate in about ten minutes. The lower oxidation products disappeared on standing, leaving only peralabamate.

## Discussion of Results

As would be expected alabamine is easily oxidized in either acid or alkaline solution. The rate of oxidation, however, is greater in acid solution. Peralabamate is the most stable form, even as weak an oxidizing agent as iodine oxidizing alabamides all the way to peralabamates. Perhalates show a steady increase in stability from perbromates through peralabamates, with the stability of perchlorates standing out as the exception. Much more work is needed to establish the mechanism and intermediate products of these reactions. The magneto-optic method lends itself beautifully to such a study.

Examination of Table I and Fig. 1 shows a difference of 0.30, 0.34 and 0.32 between successive alabamine oxygen acids. Perrhenic acid (minima at $-1.89$ and $-1.78$) is 0.05 greater than alabamous acid. Since perrhenate ion has an equivalent weight of 250.3, we estimate alabamite at 253 and a probable atomic weight of 221 for alabamine. To check this value, minima for bismuthic acid (equivalent weight of anion 257) were looked for and found at $-2.01$ and $-1.90$. That is, alabamous acid is five-twelfths of the way between perrhenic and bismuthic acids, which agrees with the above estimate.

We wish to express our thanks to Mr. J. H. Christensen and Mr. George V. Waldo for plotting the curves.

## Summary

The name alabamine and symbol Am have been suggested for element 85.

A concentrate containing $2.5 \times 10^{-6}$ g. of alabamine in the form of lithium alabamide has been prepared.

Minima have been determined for the oxygen halogen compounds.

Alabamides are easily oxidized forming hypoalabamites, alabamites, alabamates and peralabamates and their corresponding acids. Peralabamates are the most stable of these compounds.

The atomic weight of alabamine is estimated at 221.


AUBURN, ALABAMA

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## NOTES

**Iodine Monochloride in Hydrochloric Acid Solution.**—Recently[1] the contention has been made that iodine monochloride in aqueous solutions exists as $I^+$ and $Cl^-$ because iodine is more soluble in hydrochloric acid containing iodine monochloride than in the pure acid. This difference might be attributed to the increased similarity between solvent and solute, although Philbrick's view is in agreement with Abel and Halla's[2] interpretation of Sullivan's[3] potential observations. However, Forbes, Glass and Fuoss[4] have already pointed out the difficulties of reconciling such ionization with a mathematical analysis of titration curves in these solutions, and concluded that the ion $ICl_2^-$ must predominate, in agreement with Schützenberger.[5] Philbrick fails to recognize that slow hydrolysis of iodine monochloride in aqueous salt solutions, rather than ionization, better explains the slowly increasing conductance and freezing point depression observed by Sullivan[3] in freshly prepared solutions.

We have subjected these opposing views to crucial experiments. The specific conductance of an approximately one normal solution of hydrochloric acid was measured at 25° in an oil-thermostated cell, using the accurate bridge of Grinnell Jones, and found to be 0.32405 mho per cm. On adding iodine monochloride to make the solution 0.14 molal in respect to ICl, the specific conductance decreased to 0.32229 mho. This experiment proves conclusively that iodine monochloride cannot exist appreciably in the ionized state in this solution.

A transference experiment was devised to observe the direction of

[1] Philbrick, *J. Chem. Soc.*, 2254 (1930).

[2] Abegg, "Handbuch der anorganischen Chemie," 1913, IV², p. 472.

[3] Sullivan, *Z. physik. Chem.*, **28**, 523 (1899).

[4] Forbes, Glass and Fuoss, THIS JOURNAL, **47**, 2892 (1925); Forbes and Fuoss, *ibid.*, **49**, 142 (1927).

[5] Schützenberger, *Compt. rend.*, **84**, 389 (1877).

migration of the iodine during electrolysis. If iodine occurs as $I^+$ it should migrate to the cathode; if it occurs as $ICl_2^-$ it should migrate to the anode. A solution 4 *N* in hydrochloric acid and 1.6 *m* in iodine monochloride was introduced in the apparatus shown in the figure. The beakers surrounding the stopcocks contained pure hydrochloric acid. After passing 15 milliamperes through the closed stopcocks for several hours, the anode beaker, $B_1$, had a strong yellow color, while the cathode beaker, $B_2$, was colorless. Portions from both beakers were reduced with sodium bisulfite and tested for iodine with starch and chlorine water. Iodine in large amount was invariably found in the anode beaker. The test on the cathode beaker showed no trace of iodine. To show that this was not due to leakage of ICl into the anode beaker, we used fresh acid and reversed the current; again iodine was found in the anode beaker and none in the cathode beaker.

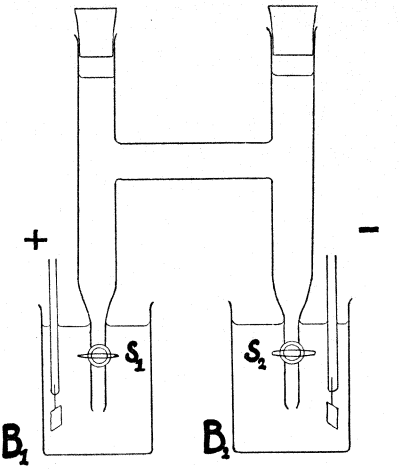

Fig. 1.

We believe that these experiments furnish strong additional evidence that the ion $I^+$ is present in negligible concentration, if at all, and that iodine monochloride forms extensively a negative complex ion with chloride ion.

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## The Preparation of Germanium Tetrabromide and Germanium Tetraiodide

**Germanium Tetrabromide.**—The only method which has been described for preparing germanium tetrabromide involves the action of bromine vapor on heated metallic germanium.[1] This procedure is laborious since it requires the preliminary preparation of elementary germanium. By modifying the method which Tabern, Orndorff and Dennis[2] used for the preparation of germanium tetrachloride it was found possible to obtain germanium tetrabromide directly from germanium dioxide and hydrobromic acid.

[1] Dennis and Hance, THIS JOURNAL, **44**, 299–307 (1922).

[2] Tabern, Orndorff and Dennis, *ibid.*, **47**, 2039 (1925).

Twenty-five grams of germanium dioxide was suspended in 250 cc. of 48% hydrobromic acid. The mixture was heated to a temperature somewhat short of the boiling point of the hydrobromic acid, and hydrogen bromide, prepared by the method given by Biltz[3] from bromine, red phosphorus and water, was passed into the solution until the acid concentration was built up to that of the constant boiling mixture. The reaction by this time had gone almost to completion and it was finished by refluxing for a short time. It is easy to tell when a sufficient amount of hydrogen bromide has been passed into the flask, since up to that point germanium tetrabromide and water (or possibly a dilute acid solution) condense together in the reflux condenser, and the germanium tetrabromide is hydrolyzed to germanium dioxide, which deposits on the condenser tube. As soon as sufficient acidity is reached in the flask, the condensate becomes acid enough to dissolve the germanium dioxide which has been formed in the condenser. When the reaction was complete, as shown by the disappearance of practically all of the germanium dioxide in the reaction mixture and the appearance of two liquid layers in the flask, the mixture was cooled, and the tetrabromide, the lower layer, was separated by means of a separatory funnel. The crude product was separated from traces of unchanged germanium dioxide by distillation. As much as possible of the hydrobromic acid still contained in the distillate was removed by holding the liquid at 26° (the freezing point of germanium tetrabromide), and evacuating the container by means of a water pump which was connected through a drying tube. The final removal of hydrogen bromide was effected by allowing the liquid to stand over solid anhydrous sodium carbonate. The germanium tetrabromide was then redistilled and the middle fraction was found to have the proper boiling point as given by Dennis and Hance.[1] The yield of purified product was approximately 90%.

**Germanium Tetraiodide.**—As in the case of germanium tetrabromide, germanium tetraiodide had been prepared only by the action of the halogen on metallic germanium, a tedious procedure. Since it had been found that the tetrabromide could be prepared with ease by the action of hydrobromic acid on a suspension of the dioxide, it seemed probable that a similar direct procedure could be used for making the tetraiodide.

Twenty-five grams of germanium dioxide was placed in a flask with 250 cc. of 57% hydriodic acid (constant boiling) and the flask was fitted with a distilling column connected with a condenser. The mixture was heated by means of an oil-bath, the temperature of which was not permitted to rise above 160°. Water was formed by the reaction

$$GeO_2 + 4HI = GeI_4 + 2H_2O$$

but by the use of the distilling column it was possible to remove water and

[3] Biltz, "Laboratory Methods of Inorganic Chemistry," translated by Hall and Blanchard, John Wiley and Sons, Inc., New York, 1928, p. 71.

keep the solution acid enough so that the reaction went in large measure to completion. As the reaction proceeded red crystals of germanium tetraiodide collected in the bottom of the flask. The tetraiodide was removed from the cold reaction mixture by filtering on a Büchner funnel and was dried in the air on a porous plate. Some unchanged germanium dioxide contaminating the tetraiodide was removed by treating the crude product with boiling carbon tetrachloride, filtering the hot solution, and crystallizing the tetraiodide from the filtrate. The yields of two separate experiments were 80 and 85% and it seems probable that stirring would increase these since the germanium tetraiodide tends to form a protective layer around the unchanged germanium dioxide.

The purified material had a melting point of 146°, the determination being made on the electric bar described by Dennis and Shelton.[4] This agrees well with the value 144° obtained by Dennis and Hance[1] using the older capillary tube method. Analyses for germanium showed that the sample was pure.

[4] Dennis and Shelton, THIS JOURNAL, **52**, 3128 (1930).

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**Note on Some Periodical Properties of Atomic Nuclei.**—In a recent paper Latimer[1] has described an interesting model of the nucleus of an atom consisting of a number of tetrahedra. Each of them, representing an $\alpha$-particle, is built of four protons located at the corners and two electrons located in the center.

Taking such tetrahedra as elements it is easy to build larger tetrahedra consisting each of 4, 10, 20, 35 and 54 elements. The numbers of protons in such nuclei will be as follows: 16, 40, 80, 140 and 216.

If we assume, now, that atomic nuclei having analogous geometrical forms must have also analogous physical properties, we must expect some periodic regularities in the system of atomic nuclei arranged according to their weight. It is possible to prove this in the following ways.

(1) Representing the number of additional nuclear electrons in a nucleus built from $\alpha$-particles as a function of the atomic weight $N$ and taking mean values for each $N$, we obtain a periodic curve, the periods corresponding well to the above-mentioned law (Fig. 1).[2]

(2) Representing the numbers of isotopes $Q$ as a function of $N$, we obtain

[1] Wendell M. Latimer, THIS JOURNAL, **53**, 981 (1931).

[2] R. A. Sonder, *Z. allgem. anorg. Chem.*, **192**, Heft 3 (1930).

also the same periodicity (Fig. 2), here are given mean values for an interval of ten values of $N$.[3]

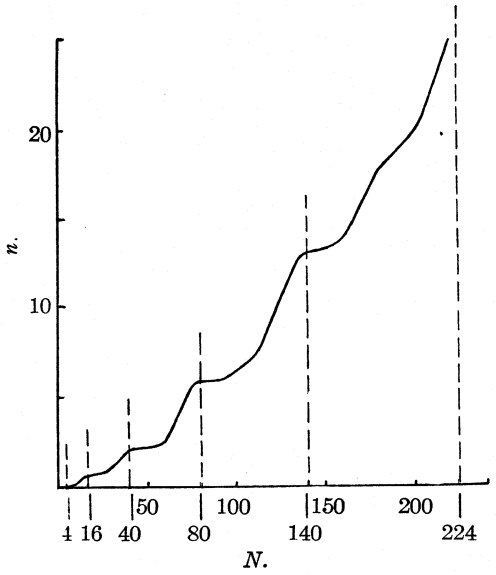


Fig. 1.—The relation between the additional electrons $n$ and the atomic weight $N$.

(3) Taking the logarithms of relative numbers of elements with even and with odd numbers of electrons as a function of $N$, and representing the

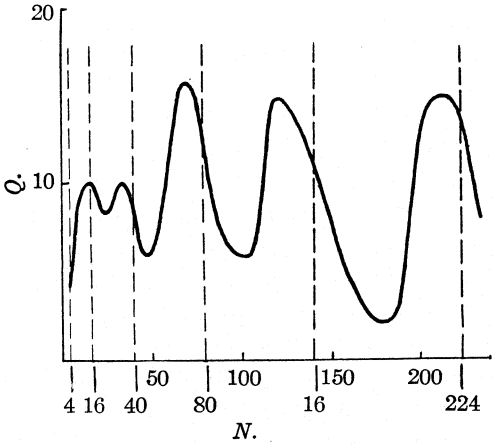


Fig. 2.—The relation between the number of isotopes $Q$ and the atomic weight $N$.

[3] G. I. Pokrowski, *Naturwiss.*, **19**, 573 (1931).

differences of these values $E$ for two neighboring elements also as a function of $N$, or of the atomic number $Z$, we obtain a curve with the same periodicity (Fig. 3).[4]

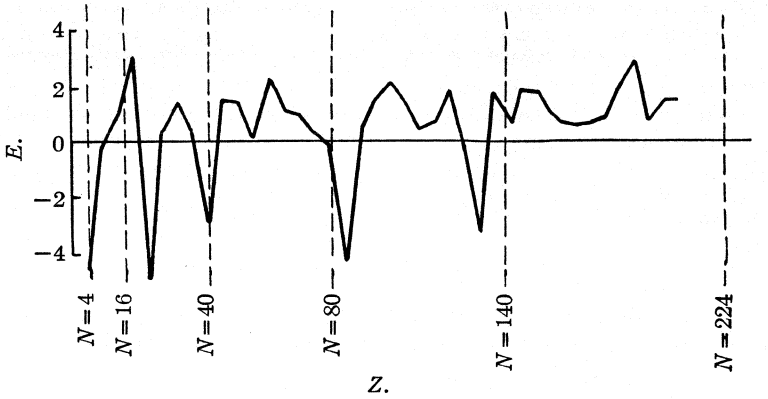


Fig. 3.—The relation between the value of $E$ and the atomic number $Z$.

Nearly the same periodicity can be deduced theoretically from de Broglie's equation. This possibility will be discussed in another place.

[4] According to experimental data given by J. and W. Noddak, *Naturwiss.*, **18**, 757 (1930).

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## Molecular Rotation in Solid Sodium Nitrate

It was shown by Kracek and his co-workers,[1] that the gradual transition in sodium nitrate at 275° is accompanied by an important change of the intensities of the diffraction lines in the powder diagrams given by this substance. They conclude "that there is no serious objection to the hypothesis of molecular rotation as an explanation of the gradual transition in sodium nitrate," this conclusion being reached by a qualitative intensity discussion, the quantitative calculation of the rotating model presenting "a most interesting difficulty."

Now the scattering power of a ring model has been calculated by Coster[2] and by Kolkmeyer[3] with a view to the possibility of electron binding rings in diamond and by one of us[4] in testing electronic models of lithium. For the case of sodium nitrate we have now performed the intensity

[1] Kracek, Posnjak and Hendricks, THIS JOURNAL, **53**, 3339 (1931).
[2] Coster, *Verslag. Akad. Wetenschappen Amsterdam*, **28**, 391 (1919).
[3] Kolkmeyer, *ibid.*, **28**, 767 (1920).
[4] Bijvoet, *Rec. trav. chim.*, **42**, 874 (1923).

calculation along these lines and reached a fair interpretation of the observed intensities, which offers a strong affirmation of the model proposed.

The calculation of the scattering power of a ring of electrons (atoms) can be made in the following way. All points in the same lattice reflection plane have the same phase. A point at a distance $d$ from this plane has a phase difference of $4\pi d \sin\theta/\lambda$ where $\theta$ represents the glancing angle.

Let the angle between the reflecting lattice plane and the plane containing the orbit of the $N$ rotating electrons (atoms) be $\alpha$ and $d\varphi$ an element of the orbit containing $N(d\varphi/2\pi)$ electrons. The distance of this element to the lattice plane is then $\rho \sin\alpha \sin\varphi$ ($\rho$ = radius of the orbit).

The diffracted amplitude is

$$\frac{N}{2\pi} e^{4\pi i d \sin\theta/\lambda}\, d\varphi$$

Integrating this over the circle we find the amplitude of the ring diffraction (phase compared with rays scattered by a point in the plane, *e. g.*, the center of the orbit)

$$\frac{N}{2\pi}\int_0^{2\pi} e^{4\pi i\rho \sin\alpha \sin\theta \sin\varphi/\lambda}\, d\varphi = NJ_0\left(4\pi\frac{\rho}{\lambda}\sin\alpha\sin\theta\right)$$

where $J_0(x)$ represents the Bessel function of the 0th order of the argument $(x)$.

This calculation is based on the very probable supposition that there is no strict phase relation between the rotation in neighboring cells.

In the case of the rotating $NO_3$ group we substitute $N = 3F(O)$ where $F(O)$ is the atomic scattering factor for oxygenium. The phase is compared with that of the center of the orbit, the nitrogen atom.

We have calculated the intensities in the usual way on the basis of the equation $I = P\dfrac{1+\cos^2 2\theta}{\cos\theta\sin^2\theta}S^2$ with

$$S = \begin{cases} 2F(\mathrm{Na}) + 2F(\mathrm{N}) + 6F(\mathrm{O})\, I_0(x) & h+k+l = 4p \\ -2F(\mathrm{Na}) + 2F(\mathrm{N}) + 6F(\mathrm{O})\, I_0(x) & h+k+l = 2p \\ 0 & h+k+l \neq 2p \end{cases}$$

Here $I_0(x)$ represents the scattering power of a ring, $x$ being equal to $4\pi(\rho/\lambda)\sin\theta\sin\alpha$; $\rho$, radius of the ring, and $\alpha$ the angle between reflecting and orbit plane.

The atomic scattering factors were taken according to James and Brindley.[5] For nitrogen the factor curve for neutral atoms was taken, as $N^{+5}$ was found not to be in accordance with the observed intensities. For oxygenium also the factor for neutral atoms is used, which only slightly differs from that of $O^{-2}$ and only for small diffraction angles.

Now it is the problem to ascertain whether it is possible to fix a value for $\rho$ which gives good agreement between calculated and observed intensities. As the Bessel function has alternating positive and negative values, it is easy to limit this value. From the fact that $32\bar{1}$ is much stronger than the corresponding neighboring reflections, it follows that the value of $\rho$ lies between 1.1 Å. and 1.65 Å. or between 2.4 Å. and 2.9 Å. The latter value

[5] James and Brindley, *Z. Krist.*, **78**, 470 (1931).

is at once excluded by 211, which is a very strong reflection. The intensities calculated with a radius $\rho = 1.15 \pm 0.05$ Å. are in very good agreement with the observed intensities (last columns, Table I). (In some films traces of reflections are reported exclusively due to oxygenium. This may be caused by uncertainty or unsteadiness of the temperature of the sample, the calculated density also indicating that the temperature of the diffracting layer is lower than that given by Kracek and his co-workers.)

TABLE I

| *hkl* | sin $\theta$ | $\alpha$ | $x$ | $J_0(x)$[a] | $\frac{1}{2}\Sigma F(0)$ | $\frac{1}{2}\Sigma F(N)$ | $\frac{1}{2}\Sigma F(Na)$ | $\frac{1}{2}S$ | $\frac{1}{2}p$ | Cont. fact. | I, calcd. | I, obs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 110 | 0.127 | 62° | 1.61 | +0.45 | 19.95 | 5.4 | −8.85 | 5.55 | 3 | 252 | 2.3 | 3.2 |
| 211 | .161 | 44° | 1.62 | +0.44 | 18.0 | 4.8 | +8.7 | 21.6 | 3 | 150 | 21.0 | >10 |
| 222 | .170 | 0° | 0.00 | +1.00 | 17.55 | 4.7 | −8.6 | 13.65 | 1 | 134 | 2.5 | 2.5 |
| $1\bar{1}0$ | .197 | 90° | 2.86 | −0.21 | 15.9 | 4.2 | +8.2 | 9.1 | 3 | 100 | 2.5 | 3.4 |
| 210 | .214 | 66° | 2.84 | −0.20 | 0.0 | 0.0 | 0.0 | 0.0 | 6 | 80 | 0.0 | <0.5 |
| 200 | .234 | 75° | 3.26 | −0.33 | 14.4 | 3.8 | −7.7 | 8.65 | 3 | 67 | 1.5 | 2.4 |
| 220 | .254 | 62° | 3.24 | −0.33 | 13.65 | 3.55 | +7.4 | 6.4 | 3 | 60 | 0.7 | 7.7 |
| 332 | .254 | 25° | 1.56 | +0.48 | 13.65 | 3.55 | +7.4 | 17.5 | 3 | 60 | 5.5 | |
| 321 | .260 | 48° | 2.78 | −0.18 | 13.5 | 3.5 | −7.3 | 6.25 | 6 | 55 | 1.3 | 2.2 |
| $2\bar{1}0$ | .302 | 63° | 3.88 | −0.40 | 0.0 | 0.0 | 0.0 | 0.0 | 3 | 42 | 0.0 | <0.5 |
| $2\bar{1}1$ | .306 | 47° | 3.24 | −0.33 | 11.25 | 2.95 | −6.6 | 7.35 | 3 | 40 | 0.7 | 1.2 |
| 433 | .316 | 20° | 1.56 | +0.48 | 11.1 | 2.9 | −6.45 | 2.25 | 3 | 38 | 0.0 | ... |
| 310 | .322 | 78° | 4.56 | −0.31 | 10.95 | 2.85 | +6.4 | 5.85 | 6 | 36 | 0.7 | 1.1 |
| 422 | .322 | 44° | 3.25 | −0.33 | 10.95 | 2.85 | +6.4 | 5.65 | 3 | 36 | 0.4 | |
| 432 | .323 | 35° | 2.67 | −0.13 | 0.0 | 0.0 | 0.0 | 0.0 | 6 | 36 | 0.0 | ... |
| 320 | .332 | 64° | 4.33 | −0.36 | 0.0 | 0.0 | 0.0 | 0.0 | 6 | 33 | 0.0 | <0.5 |
| $2\bar{1}1$ | .341 | 26° | 2.16 | +0.13 | 10.35 | 2.7 | +6.1 | 10.15 | 3 | 31 | 0.9 | 1.2 |
| 444 | .341 | 0° | 0.00 | +1.00 | 10.35 | 2.7 | +6.1 | 19.15 | 1 | 31 | 1.1 | |
| 421 | .361 | 56° | 4.33 | −0.36 | 0.0 | 0.0 | 0.0 | 0.0 | 6 | 28 | 0.0 | ... |
| 442 | .364 | 37° | 3.16 | −0.31 | 9.7 | 2.55 | −5.75 | 6.2 | 3 | 27 | 0.3 | ... |
| 431 | .377 | 53° | 4.38 | −0.35 | 9.3 | 2.45 | +5.6 | 4.8 | 6 | 25 | 0.4 | 0.5 |
| 330 | .382 | 62° | 4.88 | −0.22 | 9.15 | 2.45 | −5.5 | 5.05 | 3 | 25 | 0.2 | ... |
| $2\bar{2}0$ | .394 | 90° | 5.71 | +0.06 | 8.8 | 2.35 | +5.3 | 8.15 | 3 | 23 | 0.4 | 0.5 |
| 543 | .394 | 28° | 2.69 | −0.14 | 8.8 | 2.35 | +5.3 | 6.4 | 6 | 23 | 0.6 | to 1.0 |
| $3\bar{1}0$ | .408 | 81° | 5.83 | +0.10 | 8.55 | 2.25 | −5.15 | 2.05 | 6 | 22 | 0.0 | ... |
| 532 | .413 | 45° | 4.24 | −0.37 | 8.3 | 2.25 | −5.1 | 6.0 | 6 | 20 | 0.4 | ... |
| 554 | .422 | 15° | 1.58 | +0.47 | 8.1 | 2.2 | −4.95 | 1.05 | 3 | 19 | 0.0 | ... |
| $32\bar{1}$ | .425 | 74° | 5.88 | +0.12 | 8.1 | 2.2 | +4.95 | 8.15 | 6 | 19 | 0.8 | 1.1 |
| 420 | .428 | 66° | 5.67 | +0.05 | 8.1 | 2.2 | −5.0 | 2.4 | 6 | 16 | 0.0 | ... |
| 542 | .443 | 40° | 4.12 | −0.39 | 0.0 | 0.0 | 0.0 | 0.0 | 6 | 16 | 0.0 | ... |
| $2\bar{2}2$ | .466 | 82° | 6.70 | +0.29 | 7.4 | 2.1 | −4.3 | 0.0 | 3 | 16 | 0.0 | ... |
| 400 | .469 | 75° | 6.40 | +0.24 | 7.2 | 2.1 | +4.3 | 8.0 | 3 | 16 | 0.3 | 1.1 |
| 521 | .469 | 60° | 5.80 | +0.09 | 7.2 | 2.1 | +4.3 | 6.95 | 6 | 16 | 0.5 | |

[a] Jahnke, "Emde Funktionentafeln."

The calculated radius is somewhat smaller than that expected from the parameter value $\frac{1}{4}$ of the non-rotating oxygenium atoms, which corresponds to a distance of 1.26 Å. between nitrogen and oxygenium.

From optical data, however, a distance is calculated of 1.15 Å.[6] and even of 1.09 Å.[7]

[6] Zachariasen cited from V. M. Goldschmidt, *Geochem. V.*, **2**, 66 (1926).
[7] W. L. Bragg, *Proc. Roy. Soc.* (London), **A106**, 356 (1924).

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# POLYMERIZATION REACTIONS UNDER HIGH PRESSURE. II. THE MECHANISM OF THE REACTION

BY J. B. CONANT AND W. R. PETERSON

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Unsaturated hydrocarbons and certain aliphatic aldehydes are polymerized at room temperature by the application of very high pressure (3000–12,000 atm.)[1] In the case of isoprene the product is rubber-like; in the case of *n*-butyraldehyde the final polymer is a hard solid which reverts to the original aldehyde on standing at room temperature and atmospheric pressure. The previous work[1] showed that peroxides and ozonides were effective catalysts for both types of polymerization. However, it was concluded that peroxide catalysis was not essential since a sample of isoprene distilled in nitrogen and compressed without exposure to air polymerized at a rate only slightly less than that of material freshly distilled in air. The results of the experiments recorded in this paper have led us to revise this conclusion. We are now strongly inclined to the opinion that peroxide catalysis is essential to the polymerization and the effect of increased pressure is only to accelerate the catalytic reaction.

The evidence that peroxide catalysis is essential to the pressure polymerization of isoprene is as follows. Peroxides and ozonides have a strong positive catalytic action. Freshly distilled isoprene polymerizes at a rate only one-fifth to one-tenth of that of isoprene which has stood in the air for some days. This increased tendency to polymerize on standing is almost certainly due to the formation of peroxides from the dissolved oxygen. If peroxides (or dissolved oxygen which will form a peroxide) are essential to the polymerization, we must assume that when the isoprene was distilled in nitrogen some trace of oxygen or volatile peroxides was in the distillate. We have now strong evidence for this assumption since we have found that by adding hexaphenylethane (which reacts rapidly with oxygen) to isoprene in nitrogen and distilling, the rate of polymeriza-

[1] THIS JOURNAL, **52**, 1659 (1930).

tion of the distillate is reduced ten-fold. The material thus prepared still polymerizes under pressure (14% at 12,000 atm. in forty-eight hours); it can be argued that this represents the uncatalyzed reaction but it seems equally probable that traces of oxygen or peroxide are still present adsorbed to the glass. That very minute amounts of peroxide are sufficient for catalysis is demonstrated by the work with aldehydes which is described below.

The pressure polymerization of the aldehydes has proved to be of particular interest from the point of view of the elucidation of the mechanism of the reaction, since it is possible to prepare samples of *n*-butyraldehyde which show no evidence of polymerization after twenty-four hours at 12,000 atmospheres.[2] This is done by minimizing the time of contact of the redistilled aldehyde with the air. The aldehyde is purified through the bisulfite addition product in the usual way and then distilled carefully in nitrogen through an efficient fractionating column directly into the tube which is subsequently rapidly inserted in the press. If such a sample of carefully purified *n*-butyraldehyde is placed in an apparatus in contact with air and the oxygen absorption measured, the rate of autoxidation is found to be considerable, as shown by the results given in Table I. Samples were withdrawn from time to time and subjected to a pressure of 12,000 atmospheres for twenty-four hours at 28°; the results are given in the last column of the table. It is clear that the rate of polymerization

TABLE I

OXYGEN ABSORPTION AND RATE OF POLYMERIZATION OF *n*-BUTYRALDEHYDE

| Time, hrs. | $O_2$ absorbed per 100 cc. of aldehyde, cc. | Polymerization of sample at 12,000 atm. for 24 hr. |
|---|---|---|
| 0 | 0 | No polymerization |
| 21 | 12.6 | Liquid, viscous as glycerin |
| 50 | 24 | Very viscous liquid |
| 73 | 36 | Too viscous to pour |
| 145 | 73 | Thick paste |
| 170 | 94 | Soft solid |

parallels the oxygen absorption. Material which had stood several years in a loosely corked bottle polymerized at the fastest rate of any sample of aldehyde we were able to obtain. The butyric acid content of this aldehyde was high (14%) but this was not the effective catalyst since butyric acid added to freshly distilled butyraldehyde was without catalytic effect.

The only conclusion that can be drawn from the foregoing facts is that a very small portion of the absorbed oxygen forms some substance which has a very strong catalytic effect on the pressure polymerization. We

[2] The degree of polymerization of the aldehydes is estimated by the viscosity of the product if still liquid or roughly judged by the consistency of the paste if sufficient polymerization has occurred; quantitative results cannot be obtained.

shall designate this substance a peroxide without attempting to propose a structure for it; the amount of this catalytic substance increases with oxygen uptake parallel to the increase in butyric acid; it can therefore hardly be an intermediate between the aldehyde and the acid. One may estimate the amount of peroxide formed to correspond to not more than 1% of the absorbed oxygen, since the correlation of increased acidity and absorbed oxygen was within 1%. The minute amount formed in the absorption of 12 cc. of oxygen per 100 cc. of aldehyde would be approximately 0.12/24,500 of a mole per 100 cc. or a mole fraction of $5 \times 10^{-6}$; this amount is sufficient to bring about polymerization at an appreciable rate at 12,000 atmospheres.

Extremely sensitive tests are available for the detection of peroxide. The most sensitive involves the use of 10% ammonium thiocyanate to which a crystal of ferrous ammonium sulfate (free from the ferric salt) has been added (a peroxide develops a red color).[3] The best sample of aldehyde we could prepare distilled in nitrogen gave this test strongly. A less sensitive test is to shake the organic compound with neutral aqueous potassium iodide, a yellow to red-brown color appearing if peroxide is present. Our best samples of aldehyde freshly distilled in nitrogen gave a faint yellow on the initial shaking with the aqueous iodide solution; samples which had stood for several days and had absorbed oxygen (Table II) gave a distinctly darker color under the same conditions while older samples gave a still stronger test. The acidified potassium iodide test with starch (giving a blue color) is less sensitive (at least in the presence of aldehyde) than the test just described, samples are easily prepared which do not give this test; material which has stood for some time in the air does show peroxide by this test, however. These tests thus bear out our assumption that increasing amounts of peroxide are formed when butyraldehyde absorbs oxygen. It must be pointed out, however, that the tests are very delicate and to some extent uncertain; they must be performed under strictly comparable conditions. Even the best samples of aldehyde liberate relatively large amounts of iodine from neutral potassium iodide solution, if the mixture is shaken a few minutes in the air.

These conclusions in regard to the role of absorbed oxygen in catalyzing the polymerization of *n*-butyraldehyde are supported by the fact that other peroxides were found to be catalysts though larger amounts are necessary. Five per cent. of benzoyl peroxide dissolved in the aldehyde was sufficient to cause the formation of a hard solid in twenty-four hours at 12,000 atm. Benzaldehyde which had stood in the loosely-stoppered bottle for some days and contained 0.75 millimole of peroxide per 100 cc. (by titration), when added to the extent of 5% to freshly distilled butyral-

[3] We are greatly indebted to Mr. Edward Mallinckrodt, Jr., for calling our attention to these tests and the possibility of their application to this problem.

dehyde caused appreciable polymerization at 12,000 atm. for twenty-four hours.

**The Mechanism of the Reaction.**—In view of the facts just presented it seems to us that a peroxide is essential to the pressure polymerization of isoprene or the aliphatic aldehydes, although very minute quantities of peroxide are sufficient. We suggest that the mechanism is a series of chain reactions in the liquid initiated by the spontaneous decomposition from time to time of the peroxide. The accelerating effect of great pressures is due, according to our theory, to the orientation of the molecules of the isoprene or aldehyde into a more compact bundle in which longer reaction chains would be propagated by the spontaneous decomposition of a single peroxide molecule. It seems quite certain that as the volume of a liquid is diminished by the application of pressure, a definite orientation of the molecules is approached and we assume that this orientation is very similar to that existing in the polymer itself. This explanation corresponds with the fact that the polymer is considerably more dense than the original material (in the case of isoprene the change is from a density of 0.68 to about 0.9) and that in the polymerization of isoprene at 18,000 atmospheres, there was very little volume change during the polymerization, *i. e.*, the isoprene had been compressed very nearly to the density of the polymer before the chemical reaction started. It seems reasonable to suppose that the spontaneous decomposition of a peroxide molecule would be more effective in producing long reaction chains, the less the random motion of the molecules and the more compact and oriented they were assembled. We imagine that as each molecule becomes in turn activated by the energy originally coming from the peroxide, it unites with its neighbor, which in turn becomes active by virtue of the exothermic nature of the polymerization process. The pressure polymerization is thus to be thought of as chain reaction in which the energy is passed on in a chain and all the reacting molecules actually unite. The accelerating effect of temperature is easily explained as being due to the more frequent initiation of peroxide decompositions and hence of reaction chains. The efficiency of a given peroxide as a catalyst would depend on its instability; thus relatively large amounts of the stable benzoyl peroxide are required. The effect of negative catalysts mentioned in the previous paper would be to break the reaction chain.

The mechanism just suggested would lead to the conclusion that if a sample of aldehyde stood out of contact with air at atmospheric pressure, the spontaneous decomposition of peroxide would continue but would not result in polymerization (particularly in the case of the aldehyde since the polymer is metastable at atmospheric pressure). The decomposition of the peroxide, however, removes some of the catalyst and after long standing out of contact with air the rate of pressure polymerization

should decrease. Such was found to be the case. A sample of *n*-butyraldehyde which had taken up sufficient oxygen to polymerize to a solid after twenty-four hours at 12,000 atm. was kept in a tube with the tip under mercury and was introduced in the press without the admission of air after sixteen days. After twenty-four hours at 12,000 atm. only a thick paste resulted, showing a decrease in the rate as compared with the original material. After four months' standing out of contact with air, the same material showed no signs of polymerization after being subjected to 12,000 atm. for twenty-four hours.

The spontaneous decomposition of the peroxide at atmospheric pressure was greatly accelerated by an increase in temperature, as would be expected. Heating for twenty-eight hours at 60° out of contact with air was sufficient to destroy completely the ability to polymerize of a sample of butyraldehyde which had absorbed sufficient oxygen to polymerize to a hard solid under the usual application of pressure. A similar effect was obtained when the catalyst was an added peroxide instead of the butyraldehyde peroxide. Freshly distilled aldehyde containing 5% of benzoyl peroxide polymerizes to a hard solid under our usual conditions but after heating out of contact with air for one hundred fifteen hours, a sample showed no signs of polymerization at 12,000 atm. for twenty-four hours; after eighty-eight hours there was a very slight polymerization, while after seventy hours the polymer was a thin paste. It is interesting that oxygen was evolved during the first seventy hours of heating; this oxygen was removed before continuing the heating, the further heating was apparently necessary to decompose the aldehyde peroxide formed from the gaseous oxygen previously evolved. All these facts seem to us strong evidence in support of the mechanism just suggested.

The addition of other liquids to the aldehyde greatly diminishes the rate of polymerization, as would be expected from the point of view of our mechanism, since the chance of producing long reaction chains would be diminished. Thus, the addition of 10% by volume of absolute ethyl alcohol to butyraldehyde which had absorbed considerable oxygen perceptibly diminished the rate (a paste instead of a solid after twenty-four hours at 12,000 atm.) and 15% inhibited the polymerization to such an extent that none could be detected after twenty-four hours at 12,000 atmospheres. The amount of *n*-butyric acid necessary to produce a similar effect was 28%. With isobutyraldehyde 30% by volume of alcohol was necessary to inhibit any appreciable polymerization under our usual conditions and about 50% of isobutyric acid. Somewhat less amounts of diluents yielded pastes instead of the usual solid. Mixtures of *n*-butyraldehyde and isobutyraldehyde (both having absorbed sufficient oxygen to give high rates of polymerization) in all proportions polymerized to pastes at 12,000 atm. for twenty-four hours. The material was more

nearly solid, however, if one or the other aldehyde was present to the extent of at least 70%. These facts indicate that mixed polymers are probably formed, the aldehyde molecules being nearly interchangeable in the polymer molecule and in the reaction chains.

In addition to the pressure polymerization of the two butyraldehydes we have also found that *n*-valeric aldehyde and *n*-heptaldehyde, after distilling in the air without precautions, polymerized to thick pastes after twenty-four hours at 12,000 atm. These polymers reverted to the aldehyde on standing at room temperature and pressure as in the case of the butyraldehyde.

**Structure of the Aldehyde Polymers.**—When prepared at 12,000 atmospheres, the aldehyde polymers are hard transparent solids, if the polymerization is complete. When benzoyl peroxide is used as a catalyst or the polymerization is carried out at 4000 to 6000 atmospheres (many days being required) the polymer is not transparent but white. The completely polymerized *n*-butyraldehyde is insoluble in all the common solvents (carbon tetrachloride, chloroform, pyridine, acetophenone and cyclohexanone appear to dissolve the material very slightly). The polymer swells in benzene and toluene much as does rubber in the same solvents, but does not dissolve. The material has no melting point, since raising the temperature merely accelerates the decomposition to *n*-butyraldehyde. The spontaneous depolymerization of the polymer at atmospheric pressure is strongly catalyzed by aqueous acids or alkalies. which cause the complete depolymerization in a few minutes at 25°. The rate of decomposition of the solid itself is a function of the temperature and is greatly increased by the presence of the butyraldehyde; the process is thus autocatalytic. The material may be kept *in vacuo* over calcium chloride at 5° for considerable periods of time. The rate of decomposition of the polymer of *n*-butyraldehyde suspended in dioxane was determined by noting the change in freezing point of the solvent (11°). The results are summarized in Table II.

TABLE II

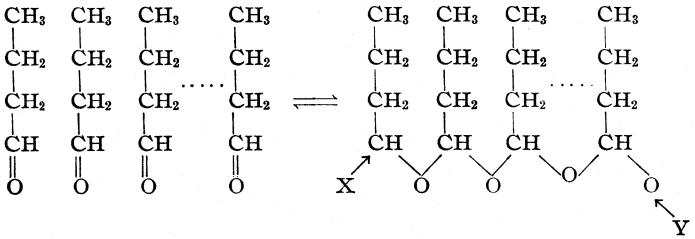
RATE OF DEPOLYMERIZATION OF *n*-BUTYRALDEHYDE POLYMER SUSPENDED IN 1,4-DIOXANE

| Temperature 50° | | | Temperature 60° | | | Temperature 70° | | |
|---|---|---|---|---|---|---|---|---|
| Time, minutes | Decomposed, % | Decomposed per min., % | Time, minutes | Decomposed, % | Decomposed per min., % | Time, minutes | Decomposed, % | Decomposed per min., % |
| 20 | 4.37 | 0.22 | 20 | 10.05 | 0.50 | 20 | 16.71 | 0.84 |
| 40 | 8.72 | .22 | 40 | 15.30 | .38 | 40 | 25.35 | .63 |
| 60 | 12.24 | .20 | 60 | 21.85 | .36 | 60 | 36.27 | .60 |
| 90 | 17.48 | .19 | 90 | 28.41 | .32 | 90 | 42.83 | .48 |
| 165 | 26.22 | .16 | 120 | 32.78 | .27 | 120 | 50.26 | .42 |
| | Average | .198 | | Average | .366 | | Average | .594 |

The percentage of decomposition was calculated on the assumption that the decrease in freezing point from time to time was due to the libera-

tion of *n*-butyraldehyde. This amounts to an assumption that there are no soluble intermediate depolymerization products. This assumption is borne out by the fact that immediately the last solid phase has disappeared there is no further depression of the freezing point in the course of time. It is clear from Table II that the rate (assuming a zero order reaction) is about double for a ten degree increase in temperature. Here there is no autocatalytic effect as there is with the solid polymer by itself.

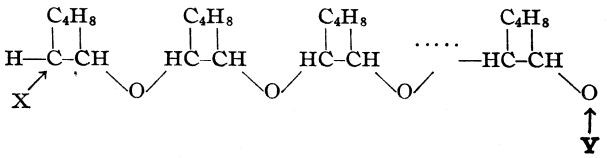
The high molecular weight of the polymer, its easy decomposition to the monomeric aldehyde and the method of its preparation lead to the conclusion that we are dealing with a higher homolog of the well-known polymers of formaldehyde. These conclusions may be represented by the following equation, the equilibrium being shifted from left to right by increased pressure. It is useless to speculate how many molecules are involved in the reaction beyond the fact that there must be very many.



The problem of the terminal valences of the long chain marked by X and Y above is unsolved. Staudinger has brought forward conclusive evidence that in the case of the polymers of formaldehyde, water, methyl alcohol or sulfuric acid have been added to the ends of the molecule depending on the method of polymerization. In the case of rubber the problem is still unsolved. We tried many experiments to attempt to place some particular group at the end of the chain. For example, if water has been added during the course of the polymerization (X = OH Y = H), it might be possible to obtain diacetates which would be stable at atmospheric pressure. We therefore treated the polymer with a variety of reagents which should react with the OH group, but without positive results. In every case either the polymer decomposed or appeared to be unaffected as judged by the unaltered ease of spontaneous depolymerization. Among the reagents tried were acetic anhydride, methyl alcohol and calcium chloride, phenyl isocyanate and bromobenzoyl bromide. Acetic anhydride was also mixed with the aldehyde before subjecting to pressure in the hope of obtaining a stable acetate, without success.

We have discovered one more type of substance which will polymerize under high pressure in the presence of peroxide. Cyclohexene oxide containing about 2% of benzoyl peroxide polymerized to a clear very viscous liquid at 12,000 atm. for one hundred sixty-eight hours; in seventy-

two hours the polymerization was hardly appreciable. The solid was obtained by evaporating off the unpolymerized material *in vacuo* at 100°. Thus prepared, the solid is a hard clear resin showing no tendency to depolymerize. It is quite soluble in benzene, chloroform, ethyl ether and amyl ether at room temperature. It is insoluble even at the boiling point in ethyl alcohol, acetone, glacial acetic acid and acetic anhydride. It did not sublime even at a pressure of $10^{-3}$ mm. of mercury and a temperature of 100°, although it was perfectly stable at this temperature. This behavior points to a high molecular weight, although by the freezing point method the apparent molecular weight in *p*-chlorotoluene was 565 and in dioxane 168. These low values are probably due to the same difficulties which have been met with in recent years in the attempts to use the freezing point method with natural products of high molecular weight. The material was unattacked by boiling concentrated hydrochloric acid or 25% alcoholic potassium hydroxide. The analyses of the most carefully dried material were as follows: calcd. for $C_6H_{10}O$: C, 73.4, H, 10.28. Found: C, 72.6, 72.2, 72.7; H, 10.1, 10.3, 10.5. It seems probable that the polymerization of this derivative of ethylene oxide is very similar to that of the aldehydes except that the polymer is stable at atmospheric pressure. The structure would be written as




## Summary

A further study has been made of the polymerization of aliphatic aldehydes and isoprene under very high pressures. It has been established that peroxides are essential to the reactions. A chain mechanism has been suggested which seems to account for all the observed facts. Attempts to stabilize the polymeric aldehydes were not successful. Cyclohexene oxide has been polymerized but with great difficulty.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF NEBRASKA AND NORTHWESTERN UNIVERSITY]

# ISOMERIC NITRO- AND AMINONAPHTHALENEARSONIC ACIDS

BY C. R. SAUNDERS[1] AND CLIFF S. HAMILTON

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The purpose of this investigation has been the study of isomeric naphthalenearsonic acids, a field in which but little work has been done. Several investigators[2] have reported the preparation of 4-amino-1-naphthalenearsonic acid, by the Béchamp[3] reaction, and certain of its derivatives, but, in most cases, the yields reported have been small. The preparations of $\alpha$- and $\beta$-naphthylarsonic acids, along with a few derivatives, have also been recorded.[4]

Attempts to repeat the preparation of 4-amino-1-naphthalenearsonic acid as carried out by O. and R. Adler[2] were unsuccessful, although Boon and Ogilvie[5] have reported that they were able to prepare, by the above method, a small amount of the arsonic acid, which they described as "an amphoteric substance persistently retaining its pink color."

According to Benda and Kahn[2] the melting point of 4-amino-1-naphthalenearsonic acid is 175°. It does not agree with the melting-point (210°) of the product obtained in this investigation, but very nearly coincides with the melting point (177°) of one of its isomers, 1-amino-2-naphthalenearsonic acid. The previous investigators did not determine the position of the arsono group, other than drawing an analogy from the reaction for the preparation of *p*-aminophenylarsonic acid. The position of the arsono group in the compounds prepared in this investigation is known beyond question. It may be that the compound already reported as 4-amino-1-naphthalenearsonic acid is really 1-amino-2-naphthalenearsonic acid, or an impure product of the 4,1-isomer.

The difficulties encountered in the separation of the isomeric mononitronaphthylamines, used as intermediates, were considerable. In most cases the methods reported in the literature were inadequate for the purpose of obtaining these substances in sufficient amounts for this work; consequently, in several instances, new methods had to be developed.

The methods of Lellmann and Remy[6] and of Sircar[7] for the separation of the isomeric mononitro-$\alpha$-naphthylamines left much to be desired. How-

[1] Parke, Davis and Company Fellow.

[2] Benda and Kahn, *Ber.*, **41**, 1676 (1908); Farb. Meister, Lucius and Bruning, German Patent 219,210; O. and R. Adler, *Ber.*, **41**, 934 (1908); Adler, German Patent 205,775.

[3] Béchamp, *Compt. rend.*, **56**, 1172 (1863).

[4] Hill and Ball, THIS JOURNAL, **44**, 2052 (1922); Michaelis and Schulte, *Ber.*, **14**, 913 (1881).

[5] Boon and Ogilvie, *Pharm. J.*, **101**, 129 (1918).

[6] Lellmann and Remy, *Ber.*, **19**, 797 (1886).

[7] Sircar, *J. Chem. Soc.*, **109**, 772 (1916).

ever, it was found that the separation could be readily accomplished by saturating an alcoholic solution of the mixture with dry hydrogen chloride. The 1-nitro-4-aminonaphthalene precipitated as the hydrochloride, leaving the 2-nitro-1-aminonaphthalene in solution.

The nitration of β-naphthylamine was first reported by Liebermann and Jacobson.[8] A modification of this method by Friedlaender and Littner[9] was a great improvement over the original method, but it was not entirely satisfactory. Small quantities of 1-nitro-2-acetylaminonaphthalene were obtained but all attempts to hydrolyze this compound led to tar formation. The use of a methyl alcohol solution of potassium hydroxide instead of an ethyl alcohol solution prevented the formation of tar. Investigations of the methods of Veselý and Jakeš[10] and of Hodgson and Kilner,[11] presented certain objectionable features so that a method was finally developed which gave good yields of 1-nitro-2-aminonaphthalene, 6-nitro-2-aminonaphthalene and 8-nitro-2-aminonaphthalene.

The corresponding arsonic acids were prepared from 2-nitro-1-aminonaphthalene, 4-nitro-1-aminonaphthalene, 1-nitro-2-aminonaphthalene and 8-nitro-2-aminonaphthalene, as well as certain derivatives. These arsenicals were analyzed for arsenic by the method of Cislak and Hamilton.[12]

## Experimental

**Nitration and Separation of the Isomeric Nitro-1-aminonaphthalenes.**—To 100 g. of α-naphthylamine and 500 cc. of glacial acetic acid was added 83 cc. of acetic anhydride. The solution was stirred rapidly with a mechanical stirrer for fifteen minutes, and then the beaker was placed in an ice-bath and the stirring continued. As soon as the acetylated material began to form a white precipitate, 53 cc. of nitric acid (sp. gr. 1.4) was added drop-wise. When the addition of the nitric acid had been completed, the solution was stirred for one-half hour and 12 g. of sodium carbonate was then slowly added. After remaining in the refrigerator overnight, the mixture was filtered and thoroughly washed with 50% acetic acid. The product consisted of a mixture of 4-nitro-1-acetylaminonaphthalene and 2-nitro-1-acetylaminonaphthalene.[6]

This mixture was placed in a three-liter round-bottomed flask and dissolved in two liters of methyl alcohol. A continuous stream of dry hydrogen chloride was then allowed to bubble through the solution. At the end of three hours a light flocculent precipitate began forming and when the precipitate became heavy enough to interfere with the passage of hydrogen chloride through the solution, the precipitate was removed by filtration. The filtrate, consisting mainly of 2-nitro-1-aminonaphthalene, was returned to the flask and the process continued. The compound which precipitated was the hydrochloride of 4-nitro-1-aminonaphthalene. This product (53 g.) was converted to the free base by neutralizing with dilute alkali and recrystallizing from hot alcohol; yield, 40 g.; m. p. 191°.[13]

[8] Liebermann and Jacobson, *Ann.*, **211**, 36 (1882).

[9] Friedlaender and Littner, *Ber.*, **48**, 329 (1915).

[10] Veselý and Jakeš, *Bull. soc. chim.*, [4] **33**, 942 (1923).

[11] Hodgson and Kilner, *J. Chem. Soc.*, **192**, 8 (1926).

[12] Cislak and Hamilton, THIS JOURNAL, **52**, 638 (1930).

[13] Liebermann, *Ann.*, **183**, 232 (1876); Kleemann, *Ber.*, 19, 338 (1886).

The filtrate, from which the 4-nitro-1-aminonaphthalene was removed as the hydrochloride, was concentrated on a water-bath to about 500 cc., decolorized with activated charcoal and filtered. The crystals which separated on standing were recrystallized twice from hot alcohol and identified as 2-nitro-1-aminonaphthalene; yield, 20 g.; m. p. 143°.[14]

**Nitration and Separation of the Isomeric Mononitro-2-aminonaphthalenes.**—To a solution of 200 g. of β-naphthylamine in 200 cc. of glacial acetic acid was added 150 cc. of acetic anhydride and the mixture stirred for fifteen minutes with a mechanical stirrer, after which the beaker containing the solution was cooled in an ice-bath and the stirring continued. In about ten minutes the acetylated material began to crystallize and at this point a further 100 cc. of glacial acetic acid was added. The temperature of the bath was then lowered by the addition of salt, and 110 cc. of concentrated nitric acid was added drop-wise over a period of three hours. After standing for several hours, the product was filtered, sucked dry and washed thoroughly with ether.[15] The product consisted of a mixture of 1-nitro-2-acetylaminonaphthalene, 8-nitro-2-acetylaminonaphthalene and an appreciable quantity of 6-nitro-2-acetylaminonaphthalene; yield of isomers, 260 g.

Hydrolysis of the mixture of isomers was effected by refluxing a solution of the product (125 g.) in alcohol (500 cc.) with concentrated hydrochloric acid (125 cc.) for four hours. The solution was then poured into three liters of cold water and the crude 1-nitro-2-aminonaphthalene filtered off, dried and recrystallized from twice its weight of hot alcohol; yield, 75 g., m. p. 127°.[16]

The filtrate, containing the soluble hydrochloride of 8-nitro-2-aminonaphthalene and 6-nitro-2-aminonaphthalene, was made alkaline to litmus with 6 *N* sodium hydroxide and immediately an orange-red precipitate formed. This was filtered off, washed with water and allowed to air dry. The product was then added to one liter of alcohol and heated to boiling on a hot-plate. A considerable portion of the material did not dissolve. After standing for a number of hours the gold colored crystals of 6-nitro-2-aminonaphthalene were filtered off, washed with cold alcohol and dried; yield, 8 g.; m. p. 203°.[10]

The filtrate from which the 6-nitro-2-aminonaphthalene had been removed was concentrated to 100 cc. and cooled in order to precipitate the dark red crystals of 8-nitro-2-aminonaphthalene. These were removed by filtration, washed with water and dried in the air; yield, 24 g.; m. p. 103.5°.[17]

### Arsonation of the Isomeric Nitro-aminonaphthalenes

**4-Nitro-1-naphthalenearsonic Acid.**—One-tenth of a mole (18.8 g.) of 1-nitro-4-aminonaphthalene was placed in a 600-cc. beaker and 200 cc. of 6 *N* hydrochloric acid added. The beaker containing the mixture was then placed in an ice-bath and equipped with a mechanical stirrer. After the contents of the beaker had dropped below 5°, a solution of sodium nitrite (8 g. of sodium nitrite in 50 cc. of water) was slowly added with constant stirring during a period of one hour. The diazonium solution was then added directly to three liters of an ice cold solution of sodium metaarsenite. The arsenite solution was prepared by dissolving 39 g. of sodium metaarsenite and a few crystals of copper sulfate in a liter of water and making up the total volume to three liters by the addition of crushed ice. The mixture was stirred rapidly by means of a me-

[14] Lellmann and Remy, *Ber.*, **19**, 802 (1886); Liebermann, *Ann.*, **183**, 246 (1876).

[15] Caution should be taken to prevent water from coming in contact with the product before washing with ether, otherwise, a tar is produced.

[16] Liebermann and Jacobson, *Ann.*, **211**, 64 (1882).

[17] Friedländer and St. Szymanski, *Ber.*, **25**, 2077 (1892).

chanical stirrer and then 220 cc. of 5*N* sodium hydroxide solution was added dropwise. The solution at this point reacted slightly alkaline to litmus paper. Stirring was continued for one-half hour longer to ensure complete coupling and then the solution was filtered. The filtrate was made acid to Congo red paper with hydrochloric acid and immediately a flocculent, light yellow precipitate of 4-nitro-1-naphthalenearsonic acid appeared. The precipitate was filtered off, reprecipitated once from *N*/2 sodium carbonate solution by means of hydrochloric acid and dried in an oven at 100°, yield, 23.7 g. (80%). The compound did not melt or decompose below 250°.

*Anal.* Calcd. for $C_{10}H_8NAsO_5$: As, 25.25. Found: As, 25.07, 25.00.

**4-Amino-1-naphthalenearsonic Acid.**—The method employed for the preparation of this compound was a slight modification of that described by Johnson and Adams.[18] It consisted essentially of the reduction of a nitro-arylarsonic acid to the corresponding aminoarylarsonic acid by means of freshly prepared ferrous hydroxide.

**2-Nitro-1-naphthalenearsonic Acid.**—Ten grams of 2-nitro-1-aminonaphthalene was dissolved in 100 cc. of hot glacial acetic acid. To this solution was added a mixture of 30 cc. of concentrated sulfuric acid and 50 cc. of water. The amine quickly separated as a fine paste. The beaker was then placed in an ice-bath and stirred with a mechanical stirrer. When the temperature of the mixture in the beaker had dropped below 5°, a solution of sodium nitrite (6.9 g. of sodium nitrite in 50 cc. of water) was added drop by drop over a period of two hours. When diazotization was complete the diazonium solution was added directly to two liters of an ice-cold solution of sodium metaarsenite (containing 30 g. of sodium metaarsenate) and a few crystals of copper sulfate. The acidity of the solution was neutralized by slowly adding 6 *N* sodium hydroxide and the solution finally made slightly alkaline by the addition of a few cc. of alkali in excess. The solution was allowed to stand overnight, filtered and the filtrate made acid to Congo red paper. A bright yellow precipitate of 2-nitro-1-naphthalenearsonic acid appeared immediately; yield, 10.2 g. (65%). The compound was reprecipitated once from dilute sodium carbonate solution with hydrochloric acid and analyzed. It proved to be practically insoluble in hot water but dissolved readily in hot alcohol from which it crystallized in well-defined yellow needles. It melted with decomposition at 202°.

*Anal.* Calcd. for $C_{10}H_8NAsO_5$: As, 25.25. Found: As, 25.11, 25.23.

**2-Amino-1-naphthalenearsonic Acid.**—The method used for the reduction of 2-nitro-1-naphthalenearsonic acid to 2-amino-1-naphthalenearsonic acid was the same as that employed for the reduction of 1-arsono-4-nitronaphthalene; a yield of 88% of the calculated amount was obtained. The compound shriveled and darkened in the m. p. tube at 174°, and finally decomposed around 216°.

*Anal.* Calcd. for $C_{10}H_{10}NAsO_3$: As, 28.09. Found: As, 28.25, 28.20.

**1-Nitro-2-naphthalenearsonic Acid.**—One-tenth of a mole (18.8 g.) of 1-nitro-2-aminonaphthalene was diazotized and coupled with sodium metaarsenite following the procedure developed for the preparation of 2-nitro-1-naphthalenearsonic acid. The compound was practically insoluble in cold alcohol but dissolved readily in hot alcohol, from which it crystallized in thin yellow plates. It melted with decomposition at 192°; yield, 20.2 g. (68%).

*Anal.* Calcd. for $C_{10}H_8NAsO_5$; As, 25.25. Found: As, 25.24, 25.24.

The monosodium salt of 1-nitro-2-naphthalenearsonic acid was yellow in color and very insoluble. A solution containing 35 g. of the arsonic acid in 500 cc. of *N*/2 sodium carbonate was made neutral to litmus paper with hydrochloric acid and on standing for

[18] Johnson and Adams, THIS JOURNAL, 45, 1312 (1923).

a short time flaky yellow crystals of the monosodium salt began to deposit on the bottom of the beaker.

**1-Amino-2-naphthalenearsonic Acid.**—This compound was prepared by reducing with ferrous hydroxide, following the directions used in the preceding reductions. One tenth of a mole gave 23.4 g. of 1-amino-2-naphthalenearsonic acid (88% yield) on reduction. It melted with decomposition at 177°.

The compound was practically insoluble in cold but very soluble in hot alcohol, acetone, glacial acetic acid and benzene. It was only slightly soluble in hot water and ether.

*Anal.* Calcd. for $C_{10}H_{10}NAsO_3$: As, 28.09. Found: As, 27.96, 27.91.

**8-Nitro-2-naphthalenearsonic Acid.**—Fifteen and four-tenths grams of 8-nitro-2-aminonaphthalene was diazotized and coupled with sodium metaarsenite in the usual manner. The solution containing the arsonic acid was filtered and acidified with hydrochloric acid. The creamy white precipitate which formed was removed by filtration and dissolved in *N*/2 sodium carbonate solution, filtered and reprecipitated by hydrochloric acid in a very pure condition; yield, 10.6 g. (43.6%). The compound did not melt or decompose under 265°.

*Anal.* Calcd. for $C_{10}H_8NAsO_5$: As, 25.25. Found: As, 25.10, 25.14.

**8-Amino-2-naphthalenearsonic Acid.**—A 5-g. sample of 8-nitro-2-naphthalenearsonic acid was reduced by means of freshly prepared ferrous hydroxide. A clear filtrate was obtained on filtering the reaction mixture which when acidified with hydrochloric acid gave a white precipitate of 8-amino-2-naphthalenearsonic acid that rapidly changed to a pink and finally to a brown color on standing a short time in contact with the air. The compound was not recovered in a pure condition. The yield of crude product was 68%.

*Anal.* Calcd. for $C_{10}H_{10}NAsO_3$: As, 28.09. Found: As, 27.58, 27.51.

**4-Benzeneazo-1-naphthalenearsonic Acid.**—To a hot solution of 10 cc. of concentrated sulfuric acid and 50 cc. of water in a 400-cc. beaker was slowly added 12 cc. of aniline with constant stirring. After the aniline had gone into solution, 150 cc. of water was added and the beaker placed in an ice-bath. When the temperature had dropped below 5°, a solution of sodium nitrite (10 g. in 50 cc. of water) was slowly added with constant stirring until a drop of the reacting mixture gave a permanent blue color to starch–iodide paper.

The diazonium solution was slowly added to a warm alcoholic solution of α-naphthylamine (15.6 g. α-naphthylamine in 600 cc. of alcohol) in a liter beaker. The mixture was stirred for one-half hour and then poured into two liters of water. Immediately a brown amorphous product precipitated. The reaction proceeded almost quantitatively.

One-tenth of a mole (35.6 g.) of the dye thus formed was dissolved in 100 cc. of glacial acetic acid in a 600-cc. beaker and cooled rapidly with constant stirring. To this solution was added 30 cc. of concentrated sulfuric acid and 60 cc. of water. The beaker was then placed in an ice-bath and a solution of sodium nitrite (10 g. in 50 cc. of water) was added drop-wise over a period of two hours. At the end of this time diazotization was assumed to be complete and the diazonium solution was added directly to two liters of an ice-cold solution of 39 g. of sodium metaarsenite containing a few crystals of copper sulfate. The solution was gradually neutralized by the addition of 6*N* sodium hydroxide and then a few cc. in excess was added. The resulting mixture was filtered and the filtrate made acid to Congo red paper with hydrochloric acid. A red precipitate formed immediately which recrystallized from hot alcohol in the form of reddish-yellow plates. The yield, however, was very small (8%).

*Anal.* Calcd. for $C_{16}H_{13}N_2AsO_3$; As, 21.07. Found: As, 20.90, 21.02.

TABLE I

DERIVATIVES OF AMINONAPHTHALENEARSONIC ACIDS

| Name, -naphthalenearsonic acid | Yield, % | M. p., °C. | Arsenic analyses, % Calcd. | Found |
|---|---|---|---|---|
| 4-Acetylamino-1 | 90 | 271 dec. | 24.27 | 24.15 |
| 4-Carbethoxyamino-1 | 90 | 250 | 22.12 | 22.03 |
| 4-β-Hydroxyethyl-1 | 65 | 250 | 24.11 | 24.03 |
| 1-Acetylamino-2 | 72 | 240–245 dec. | 24.27 | 24.24 |
| 1-Carbethoxyamino-2 | 95 | 191 dec. | 22.12 | 21.93 |


## Summary

Better methods have been developed for the separation of the isomeric nitroaminonaphthalenes formed by the nitration of α- and β-naphthylamines, thus permitting their preparation on a large scale.

The nitroaminonaphthalenes have been arsonated and the products, 4-nitro-1-naphthalenearsonic acid, 2-nitro-1-naphthalenearsonic acid, 1-nitro-2-naphthalenearsonic acid, and 8-nitro-2-naphthalenearsonic acid have been isolated, the last three for the first time.

The isomeric nitronaphthalenearsonic acids have been reduced to the corresponding aminonaphthalenearsonic acids and several derivatives of these have been prepared.


LINCOLN, NEBRASKA

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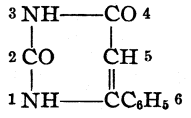
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# ULTRAVIOLET ABSORPTION SPECTRA OF SOLUTIONS OF SOME SUBSTITUTED PHENYLURACILS[1]

BY JANET EVANS

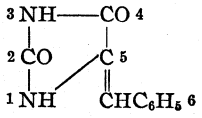
RECEIVED AUGUST 17, 1931 PUBLISHED FEBRUARY 5, 1932

Uracil and hydantoin are quite similar in many ways. Both are urea derivatives, both form sodium salts and both can be alkylated. A comparison of the alkylation products obtained from 6-phenyluracil[2] and the isomeric 5-benzalhydantoin[3] shows analogous changes in physical properties such as melting point and solubility.




6-Phenyluracil

and




5-Benzalhydantoin

In the benzal- and anisalhydantoin series, considerable differences in the

[1] Constructed from a dissertation presented by Janet Evans to the Faculty of the Graduate School of Yale University, in June, 1929, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Evans and Johnson, THIS JOURNAL, **52**, 4993 (1930).

[3] Hahn and Evans, *ibid.*, **50**, 806 (1928).

ultraviolet absorption spectra of alkylated compounds occur, so that hydantoins having a substituent in the N-1 position can be readily distinguished from hydantoins of the same series which are unsubstituted or substituted only in the N-3 position.[3,4,5] The absorption curves for alcohol solutions of 5-benzalhydantoin and methyl-5-benzalhydantoin-N-3-acetate are almost identical and show a single broad absorption band with a maximum about $1/\lambda = 32{,}000$ cm.$^{-1}$ but these curves differ from those of the two isomeric N-1-methyl-5-benzalhydantoin-N-3-acetic acids. An earlier study of the derivatives of anisalhydantoin[6] showed an exactly parallel relationship between the ultraviolet absorption spectra of the N-3-substituted N-5-anisalhydantoins and the disubstituted compounds and it was further shown that the type of substituent made little if any difference.

Reasoning by analogy, since hydantoins and uracils have so much in common, it should also be possible to differentiate between N-1 and N-3 substitution products of uracils having an aryl group in the 6-position, if the structure of one compound is definitely known or if there are isomeric N-1 and N-3 substituted compounds.

In order to determine whether absorption spectra can be used to distinguish N-1 and N-3 substituted uracils, measurements of the ultraviolet absorption spectra of some phenyluracils have been made.

## Experimental

The preparation, properties and proof of structure of these uracils have been described in a previous paper.[2] The samples which were used had been recrystallized four times from alcohol or until the melting point remained constant and finally from alcohol which was specially prepared for spectrographic work.[7] Hundredth molar solutions were made by dissolving the calculated amount in 50 cc. of alcohol. These solutions were then diluted to 0.0002, 0.0001 and 0.00002 *M*.

The absorption spectrum measurements were made with a Hilger quartz spectrograph (E2) using an iron spark as a source of light. The sparking apparatus consisted of a 0.25 kilowatt transformer and condenser of approximately 0.03 m. f. capacity as recommended by Hilger. The spark gap between the rectangular iron electrodes (2 mm. by 3 mm.) was kept at 2 mm. The absorbing medium was contained in small Baly absorption tubes of clear fused quartz with ground quartz connections. Lumière and Jougla photographic plates were used throughout.

The extinction coefficients were determined by the photographic method

[4] Carr and Dobbrow, THIS JOURNAL, **47**, 2961 (1925).

[5] Maclean, Thesis, Mount Holyoke College, 1926.

[6] Carr, Report at Richmond meeting of the American Chemical Society, April, 1927.

[7] Castille and Henri, *Bull. soc. chim. biol.*, **6**, 301 (1924).

of comparison spectra developed by Henri.[8] The readings were plotted using the logarithm of the extinction coefficient as ordinate and the reciprocal of the wave length or the wave number in cm.$^{-1}$ as abscissa. The extinction coefficient was calculated from the experimental data using the usual formula

$$\epsilon = \frac{0.9}{d \times M} \log \frac{T}{T_0}$$

in which $\epsilon$ is the extinction coefficient; 0.9 is a constant depending on the properties of the photographic plate; $d$ is the thickness in centimeters of the solution through which the light passes; $M$ is the concentration in moles per liter of solution; $T$ is the time of the exposure through the solution; and $T_0$ the time of the exposure through the same thickness of pure alcohol for comparison. $T_0$ was ten seconds throughout; $T$ was forty or sixty seconds. The thickness $d$ was varied from 0.6 to 6 cm.

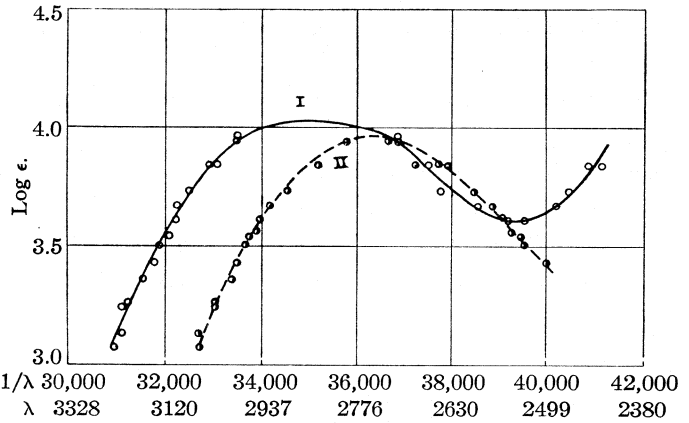



Plate 1.—I, ○, 6-phenyluracil; II, ◑, N-1-3-dimethyl-6-phenyluracil.

## Discussion of Results

The absorption curves (Plates 1, 2, 3) of non-substituted 6-phenyluracil (Curve I) and the two N-3 substituted derivatives, N-3-methyl-6-phenyluracil (Curve III) and ethyl-6-phenyluracil-N-3-acetate (Curve V), are almost identical. In each case the maximum of the band is at $1/\lambda$ = 35,000 cm. The N-1-methyl-6-phenyluracil (Curve IV) and the two disubstituted compounds, methyl-N-1-methyl-6-phenyluracil-N-3-acetate (Curve VI) and N-1,3-dimethyl-6-phenyluracil (Curve II), also give almost identical curves but these show a decided difference from the curves of the preceding group. The band is shifted toward the ultraviolet, the maximum being about 36,250 cm.$^{-1}$. Also the bands of Curves II, IV and VI are somewhat narrower and slightly more persistent than those of

[8] Henri, "Études de Photochemie," Paris, 1919, p. 5.

Curves I, III and V, although the intensity is less. Evidently substitution for the hydrogen in the N-1 position, whether the hydrogen in the N-3 position has been replaced by a substituent group or not, has considerable

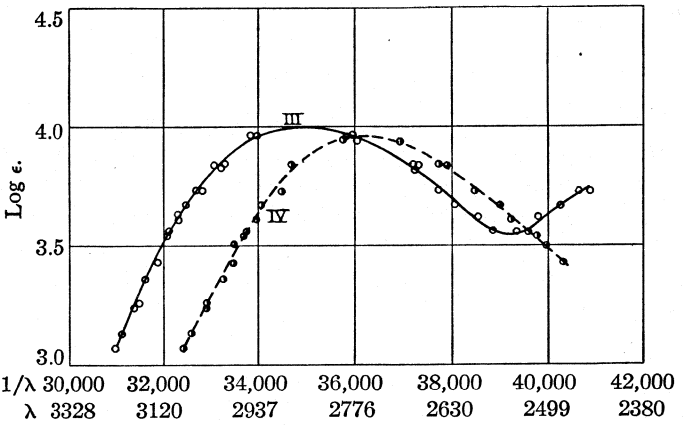



Plate 2.—III, ○, N-3-methyl-6-phenyluracil; IV, ◑, N-1 methyl-6-phenyluracil.

influence on the absorptive power of the molecule. Here, as in the hydantoin series, the type of substituent has little effect on the absorption. Therefore, it should be possible to determine the position of the substituent

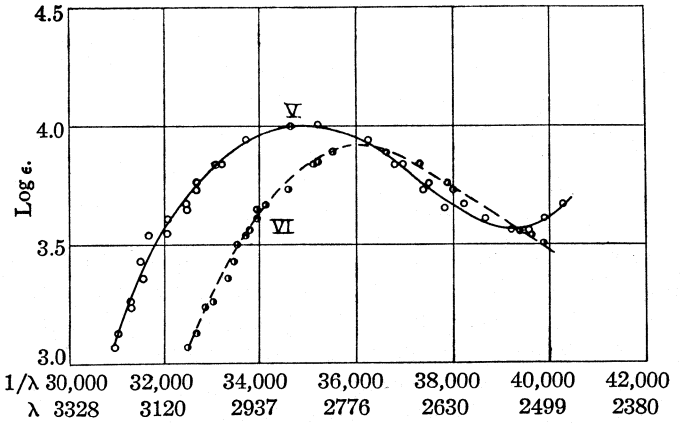



Plate 3.—V, ○, ethyl-6-phenyluracil-N-3-acetate; VI, ◑, methyl-N-1-methyl-6-phenyluracil-N-3 acetate.

group in a derivative of 6-phenyluracil by comparison of its absorption spectrum with those already studied. It may also be predicted that N-1 and N-3 derivatives of a uracil having any aryl group in position 6 can be differentiated by means of absorption spectra and that the com-

pounds whose absorption band lies farthest in the ultraviolet may be considered N-1 substituted compounds.

It has been stated that the properties of 6-phenyluracil are to some extent like those of 5-benzalhydantoin. However, 6-phenyluracil does not react so readily as the 5-benzalhydantoin nor is the yield of alkylated product so great. The double bond cannot be reduced at all by the means by which 5-benzalhydantoin is reduced easily. Comparison of their absorption curves shows that both have the same type of selective absorption but the band of 6-phenyluracil (Curve I) occurs much farther out in the ultraviolet ($1/\lambda = 35{,}000$ cm.$^{-1}$) and is less intense ($\log \epsilon = 4.0$) than that of 5-benzalhydantoin[3] ($1/\lambda = 31{,}750$ cm.$^{-1}$) and ($\log \epsilon = 4.35$). The same relation is maintained between the absorption bands of the other pairs of isomers. This result is in accordance with Henri's conclusion[9] that the most reactive substances possess the strongest absorption and the absorption bands of a compound are shifted toward the visible as chemically reactive groups are introduced.

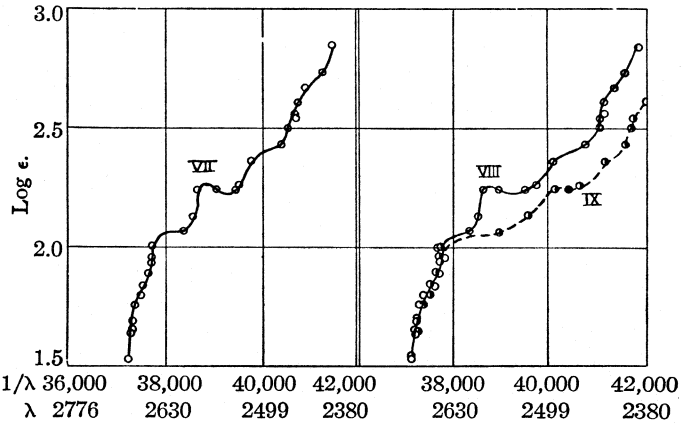



Plate 4.—VII, ○, ethyl-N-1-methyl-6-phenylhydrouracil-N-3-acetate; VIII, ○, N-1-methyl-6-phenylhydrouracil; IX, ◑, N-3-methyl-6-phenylhydrouracil.

The groups which absorb light, *i. e.*, chromophoric groups in phenyluracil and in benzalhydantoin are the benzene ring, the double bond between the two carbon atoms 5 and 6, and the two carbonyl groups. In phenyluracil the double bond is in the ring, whereas in benzalhydantoin it is outside. Experimental results, in general, show that a double bond in the ring is less reactive than one in a chain, and these results appear to show that it confers less absorptive powers on the molecule.

The absorption curve of ethyl-N-1-methyl-6-phenylhydrouracil-N-3-acetate (Plate 4, Curve VII) is very similar to that of methyl-N-1-methyl-5-

[9] Henri, Ref. 8, pp. 174, 187.

benzylhydantoin-N-3-acetate.[3] Both show only a tendency to band formation rather than a discrete band and this "step-out" begins at approximately $1/\lambda = 38{,}000$ cm.$^{-1}$ and $\log \epsilon = 2.0$ for each. As noted above, the corresponding unsaturated compounds, methyl N-1-methyl-6-phenyluracil-N-3-acetate and N-1-methyl-5-benzalhydantoin-N-3-acetic acid, do not show this similarity. Reduction of the double bonds of two unsaturated compounds having the same chromophoric groups but markedly different absorptive powers has produced two compounds of very similar absorptive power although one contains a six- and one a five-membered ring. This also indicates the great difference between the influence on the absorption of a double bond outside a ring and one in the ring.

The curves of N-1-methyl-6-phenylhydrouracil (Curve VIII) and ethyl-N-1-methyl-6-phenylhydrouracil-N-3-acetate (Curve VII) are alike and have "step-outs" which are slightly narrower than that of N-3-methyl-6-phenylhydrouracil (Curve IX) but this difference is not sufficiently characteristic to be used for purposes of identification.

This work has been done at Mount Holyoke College through the courtesy of Professor Emma P. Carr to whom the author is deeply indebted for the use of the spectrograph and for valuable advice. Acknowledgments are also due to Professor Treat B. Johnson at whose suggestion the investigation was undertaken, to Dr. J. B. Austin for constructive interest, and to Miss Edith R. Barstow for help in preparing the manuscript.

## Summary

1. The ultraviolet absorption spectra of 6-phenyluracil, N-3-methyl-6-phenyluracil, ethyl-6-phenyluracil-N-3-acetate, N-1-methyl-6-phenyluracil, N-1-3-dimethyl-6-phenyluracil, methyl-N-1-methyl-6-phenyluracil-N-3-acetate, N-1-methyl-6-phenylhydrouracil, N-3-methyl-6-phenylhydrouracil, and ethyl-N-1-methyl-6-phenylhydrouracil-N-3-acetate have been measured.

2. The absorption spectra of those uracils having a substituent in the N-1 position have been found to differ from those of uracils which are non-substituted or have substituents in the N-3 position.

3. This difference can be used to distinguish N-1 substituted from N-3 substituted uracils of the type of 6-phenyluracil.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

# ABNORMAL REACTIONS OF BENZYLMAGNESIUM CHLORIDE[1]

BY PAUL R. AUSTIN AND JOHN R. JOHNSON

RECEIVED AUGUST 17, 1931 PUBLISHED FEBRUARY 5, 1932

Nearly thirty years ago Tiffeneau and Delange[2] observed that the action of formaldehyde on benzylmagnesium chloride produced *o*-tolylcarbinol instead of the expected benzylcarbinol. Since that time, owing to the widespread development of the use of organomagnesium halides in synthesis, the action of a variety of substances on benzylmagnesium chloride has been reported. Although many reactants (carbon dioxide, acetone and many ketones, acetals and esters) have been shown to produce the normal products, another group of reactants (benzaldehyde, ethyl formate, ethyl chlorocarbonate, halogen methyl alkyl ethers and ethylene oxide) has been found to yield products of rearrangement, usually *o*-tolyl derivatives. It has also been observed that rearrangement occurs with other Grignard reagents that show a structural resemblance to benzylmagnesium chloride.[3] The present investigation, dealing with the action of various reagents upon benzylmagnesium chloride, was undertaken with the object of developing certain generalizations concerning the nature of the reactants that lead to products of rearrangement and of elucidating the mechanism of the reaction.

An important feature of the previously reported reactions of benzylmagnesium chloride is that certain reagents produce both the normal and abnormal products, while with others only one type of product has been observed.[4] Superficially, this behavior is similar to that of the sodium derivatives of certain enols, which may react to produce substances in which substituents are introduced on the $\alpha$-carbon atom or the oxygen atom, or both of these.

Several of the earlier investigators who worked with benzylmagnesium chloride, not anticipating an unusual reaction, reported results that have

[1] This paper is an abstract of a portion of a thesis submitted by Paul R. Austin to the Graduate Faculty of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1930.

[2] Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903).

[3] (a) Carré, *Bull. soc. chim.*, [4] **5**, 487 (1909); [4] **7**, 841 (1910); (b) Chelintzev and Karmanov, *J. Russ. Phys.-Chem. Soc.*, **47**, 161 (1915); *Chem. Abstracts*, **9**, 1472 (1915); (c) Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927); (d) Gilman and Kirby, *ibid.*, **51**, 3475 (1929); (e) Gilman and Harris, *ibid.*, **53**, 3541 (1931).

[4] A serious obstacle in studying the reaction mechanism is the difficulty of isolating all of the products of any reaction. It is almost impossible to state with certainty that none of a particular product is formed in a reaction. In many instances complications arise from the reaction of the initial products with a second or third molecule of the organomagnesium halide. This situation obtains in the case of esters, acid halides and anhydrides.

proved to be erroneous or have left some doubt as to the structure of the products. The case of ethyl chlorocarbonate is a striking example of this. Houben[5] reported that benzylmagnesium chloride acted upon ethyl chlorocarbonate to produce ethyl phenylacetate (43% yield) and tribenzylcarbinol (10% yield). Recently, Gilman and his collaborators[6] have shown that ethyl *o*-toluate is produced in this reaction together with a relatively small amount of ethyl phenylacetate. The latter result throws doubt on the structure of the alcohol reported by Houben as tribenzylcarbinol, since one might expect *o*-tolyldibenzylcarbinol to be produced by the action of benzylmagnesium chloride on ethyl *o*-toluate.

The present study confirmed completely the findings of Gilman and Kirby, that ethyl *o*-toluate and ethyl phenylacetate are formed in this reaction, and showed that the alcohol described by Houben is actually tribenzylcarbinol. This result indicated that the initial products, ethyl *o*-toluate and ethyl phenylacetate, differ greatly in their tendency to react further with benzylmagnesium chloride. Ethyl phenylacetate, the normal product, evidently reacts with benzylmagnesium chloride much more readily than ethyl *o*-toluate, the product of rearrangement. This difference in reactivity explains similar observations in other cases where the initial products can react further with the Grignard reagent. The following experiment confirmed the predicted difference in reactivity of the initial products. An ethereal solution of equimolar quantities of ethyl *o*-toluate and ethyl phenylacetate was treated with a dimolar quantity of benzylmagnesium chloride. A large part of the ethyl *o*-toluate was recovered unchanged (72%), together with a small amount of ethyl phenylacetate (7%), and tribenzylcarbinol was produced in large quantity (71% of the theoretical).[7]

In the course of a study of the preparation of ketones by the action of organomagnesium halides on acid chlorides,[8] it was observed that acetyl chloride reacts with benzylmagnesium chloride to produce an *o*-tolyl ketone (*o*-methylacetophenone) instead of the expected benzyl ketone. Subsequently, it was found that acetic anhydride and benzoyl chloride react with benzylmagnesium chloride in similar fashion to produce *o*-tolyl

[5] Houben, *Ber.*, **36**, 3087 (1903).

[6] Gilman, Kirby, Fothergill and Harris, *Proc. Iowa Acad. Sci.*, **34**, 221 (1927); *Chem. Abstracts*, **22**, 450 (1928).

[7] It seems likely that the action of benzylmagnesium chloride upon ethyl *o*-toluate does not proceed beyond the formation of the ketone, *o*-tolyl benzyl ketone. This result, as well as the preferential reaction of ethyl phenylacetate, is in agreement with observations of Conant and Blatt [THIS JOURNAL, **51**, 1227 (1929)] on the action of Grignard reagents upon branched chain compounds.

[8] Johnson and Dawson, a preliminary paper presented at the Seventh Midwest Regional Meeting of the American Chemical Society, University of Chicago, May 28, 1927.

derivatives. The case of benzoyl chloride is strictly analogous to that of ethyl chlorocarbonate; the principal products of the reaction are *o*-methylbenzophenone and phenyldibenzylcarbinol. Evidently in this instance also, the initial products (*o*-tolyl phenyl ketone and benzyl phenyl ketone) differ greatly in their tendency to react with benzylmagnesium chloride. Only the benzyl derivative reacts further, and produces phenyldibenzylcarbinol.

The results mentioned above, together with a number of other experimental results observed with benzylmagnesium chloride, are summarized in Table I. Nearly all of the reactants listed as abnormal, lead to the production of *o*-tolyl[9] *and* benzyl derivatives. The list of normal reactants is not a complete compilation but a general summary of the normal reactions of benzylmagnesium chloride.

TABLE I

REACTIONS OF BENZYLMAGNESIUM CHLORIDE

| Abnormal reactants | Normal reactants |
|---|---|
| Formaldehyde | Paraldehyde |
| Benzaldehyde | Alkyl and aryl ketones |
| *p*-Methoxybenzaldehyde | Acetals and ethyl orthoformate |
| Ethylene oxide | Ethyl acetate, benzoate and carbonate |
| Alkyl chloromethyl ethers | Carbon dioxide |
| Ethyl and methyl chlorocarbonate | Epichlorohydrin and chloroacetone |
| Ethyl formate | Allyl iodide |
| Acetyl and benzoyl chloride | Mercuric chloride |
| Acetic and chloroacetic anhydride | Phenyl isocyanate |
| | Alkyl *p*-toluene sulfonates |

An inspection of this summary shows that the abnormal reactants do not form a homogeneous group. While it is unwise to draw broad generalizations from the limited experimental data, one is led to the conclusion that acid chlorides and anhydrides favor an abnormal reaction, as do formaldehyde and its derivatives (R—O—$CH_2X$), and esters of formic acid. The anomalous behavior of aromatic aldehydes is striking; Schmidlin and Garcia-Banùs[10] found that the slow addition of benzaldehyde to benzylmagnesium chloride gave as much as 95% of the normal product (phenylbenzylcarbinol), whereas the reverse addition gave only 30% of the normal product and 70% of diphenylisochromane. In the present study the organomagnesium halide was always added slowly to an excess of the reactant.

Abnormal reactions similar to those of benzylmagnesium chloride have been observed with 3,5-dimethylbenzylmagnesium chloride[3a] and α-naphthylmethylmagnesium chloride.[3d] Gilman and Harris[3c] have shown

[9] Some of the *p*-tolyl derivative is stated to be formed from benzaldehyde, alkyl chloromethyl ethers, ethyl formate and ethylene oxide Ref. 3 (d).

[10] Schmidlin and Garcia-Banùs, *Ber.*, **45**, 3193 (1912).

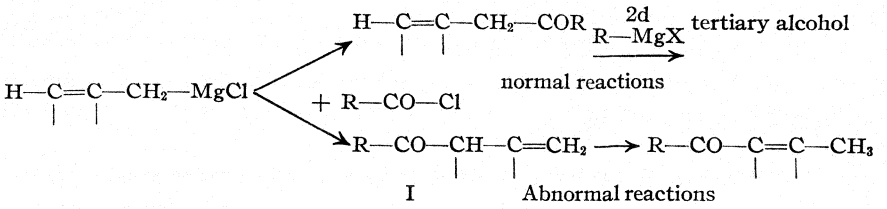
that the reaction between cinnamyl chloride, magnesium and carbon dioxide gives rise, likewise, to a product of rearrangement. Since the abnormal reaction involves the ortho positions of the benzyl group, it seemed of interest to investigate the behavior of substituted benzylmagnesium halides with groups in the ortho position. For this purpose 2-chloro- and 2,6-dichlorobenzylmagnesium chloride were chosen, and their behavior toward carbon dioxide, methyl chlorocarbonate, acetic anhydride and acetyl chloride was observed. The results are shown in Table II, together with the corresponding observations on benzylmagnesium chloride. From these and other available data, it is clear that the rearrangement (abnormal reaction) depends upon the nature of the reactant *and* of the organomagnesium halide. From the standpoint of the reactants, it appears that the tendency to produce rearrangement decreases in the order: acetyl chloride > acetic anhydride > methyl chlorocarbonate > carbon dioxide. In the Grignard reagents, the tendency to undergo rearrangement appears to decrease to some extent with the introduction of one ortho substituent and decreases further by the introduction of two ortho substituents. In the latter, the rearrangement necessarily leads to a *p*-tolyl derivative.

TABLE II

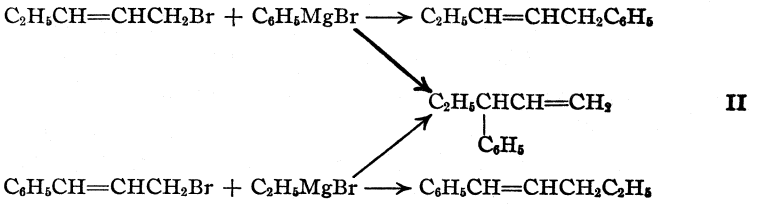
REACTIONS OF BENZYL- AND ORTHO-SUBSTITUTED BENZYLMAGNESIUM CHLORIDES

| Reactant | Organomagnesium chloride | | |
|---|---|---|---|
| | Benzyl- | 2-Chlorobenzyl | 2,6-Dichlorobenzyl- |
| $CO_2$ | *Normal*<br>$C_6H_5CH_2COOH$<br>Phenylacetic acid | *Normal*<br>$2\text{-}ClC_6H_4CH_2COOH$<br>2-Chlorophenylacetic acid | *Normal*<br>$2,6\text{-}Cl_2C_6H_3CH_2COOH$<br>2,6-Dichlorophenylacetic acid |
| $CH_3OCOCl$ | *Rearrangement*<br>$2\text{-}CH_3C_6H_4COOCH_3$<br>Methyl *o*-toluate | *Normal*<br>$2\text{-}ClC_6H_4CH_2COOCH_3$<br>Methyl 2-chlorophenylacetate | *Normal*<br>$2,6\text{-}Cl_2C_6H_3CH_2COOCH_3$<br>Methyl 2,6-dichlorophenylacetate |
| $(CH_3CO)_2O$ | *Rearrangement*<br>$2\text{-}CH_3C_6H_4COCH_3$<br>2-Methylacetophenone | *Rearrangement*<br>$2,3\text{-}(CH_3)ClC_6H_3COCH_3$<br>2-Methyl-3-chloroacetophenone | *Normal*<br>$2,6\text{-}Cl_2C_6H_3CH_2COCH_3$<br>2,6-Dichlorophenylacetone |
| $CH_3COCl$ | *Rearrangement*<br>$2\text{-}CH_3C_6H_4COCH_3$<br>2-Methylacetophenone | *Rearrangement*<br>$2,3\text{-}(CH_3)ClC_6H_3COCH_3$<br>2-Methyl-3-chloroacetophenone | *Rearrangement*<br>$4,3,5\text{-}(CH_3)Cl_2C_6H_2COCH_3$<br>4-Methyl-3,5-dichloroacetophenone |

In the organomagnesium halides that undergo abnormal reaction, a triad system $H-\overset{\gamma}{C}=\overset{\beta}{C}-\overset{\alpha}{CH_2}-MgX$ is present; the rearrangements result in the introduction of the entering group in the $\gamma$-position instead of the $\alpha$-position, and a migration of hydrogen in the reverse direction, from the $\gamma$-position to the $\alpha$-position. With an acid chloride, for example, the following reactions can be written.




The formulation of the intermediate product I, resolves the rearrangement into two steps. The plausibility of this point of view is enhanced by experimental evidence from studies by Prévost,[11] who showed that the action of Grignard reagents upon halides of the type R—CH=CH—$CH_2Br$, produced compounds corresponding in structure to the intermediate compound I.




In the examples cited, 3-phenylpentene-1 (II) appears as the abnormal product and represents the first step in the mechanism formulated above. In this compound, the phenyl group does not sufficiently activate the hydrogen on the $\gamma$-carbon atom to cause a migration to the $\alpha$-position. An acyl group, in the structure I, causes the $\gamma,\alpha$-migration of hydrogen to occur easily and in the final product the double bond forms a conjugated system with the carbonyl group. The second step of the abnormal reaction ($\gamma,\alpha$-migration of hydrogen) appears to be analogous to the well known keto ⟶ enol transformations. The effect of variations of R in the system $RCH_2CO$— is parallel to the effect in the system RCHCH=$CH_2$; in both systems the activating effect of the R group diminishes in the order: acyl > phenyl > alkyl.

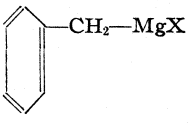
The effect of substituents in the triad system upon the first step of the rearrangement ($\alpha,\gamma$-migration of the entering group) is more obscure. In the system A—C≡C—$CH_2$—B, the nature of the substituents A and B, as well as that of the reactant, have an important effect on the inherent tendency to undergo abnormal reaction. In certain triad systems (cinnamyl bromide) abnormal reactions occur when B is a halogen atom, or the MgX residue; in others (benzyl chloride and iodide) abnormal reactions do not occur when B is a halogen atom,[12] but do occur when B is the MgX

[11] Prévost, *Ann. chim.*, [10] **10**, 121 (1928); Prévost and Daujat, *Bull. soc. chim.*, [4] **47**, 588 (1930).

[12] We have not been able to observe the formation of *o*- or *p*-tolyl derivatives in reactions of benzyl chloride and benzyl iodide. Mr. E. W. Scott in this Laboratory has

residue. From these comparisons it appears that an MgX residue in the $\alpha$-position produces a greater inherent tendency to undergo abnormal reaction than a halogen atom, and that a system containing a phenyl group in the $\gamma$-position is more prone to undergo rearrangement than one in which the $\beta$- and $\gamma$- atoms form part of a benzene ring.

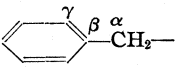
Of the theories that have been proposed for the mechanism of the formation of abnormal products from benzylmagnesium chloride, the hypothesis of Schmidlin and Garcia-Banùs[10] appears to be the most satisfactory. They assume a dynamic isomerism between the normal form and an *o*-quinonoid form (III)[13]



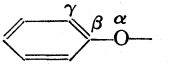

Normal form *o*-Quinonoid form III

The suggestion of a transformation to *o*-tolylmagnesium chloride appears to be untenable, since this condition would require the formation of *o*-tolyl derivatives with all reactants or a dynamic isomerism between benzyl and *o*-tolyl magnesium halides. In order to test this point, a careful examination was made of the action of carbon dioxide on benzylmagnesium chloride and on *o*-tolylmagnesium bromide. All of the fractions and all of the filtrates were examined minutely in each case, and it was found that no *o*-toluic acid was produced from benzylmagnesium chloride nor was any phenylacetic acid produced from *o*-tolylmagnesium bromide.

Tiffeneau and Delange[2] have compared this rearrangement with certain abnormal reactions of sodium phenolate. In the phenoxyl group, there is present a triad system similar to that of the benzyl group, except that an oxygen atom takes the place of the $\alpha$-methylene group.




Benzyl group




Phenoxyl group

The C-alkylation of phenols as well as many aliphatic enols may be accounted for on the basis of addition of the reactant at the $\beta,\gamma$-double bond,[14] a mechanism that does not require the postulation of a tautomeric form of the enol. Although the addition theory of Michael[15] has been

effected reactions between benzyl iodide and sodium cyanide under the same conditions that give rise to an abnormal reaction with $\alpha$-furfuryl chloride [THIS JOURNAL, **52**, 1284 (1930)], but was unable to detect any *o*- or *p*-tolunitrile in the product.

[13] Stewart, "Recent Advances in Organic Chemistry," Longmans, Green and Co., London, 5th ed., 1927, Vol. II, p. 295, suggests a similar *p*-quinonoid structure to account for the red color of sodium benzyl.

[14] Claisen, *Ann.*, **442**, 222 (1925).

[15] Michael, *J. prakt. Chem.*, [2] **37**, 486 (1888); **46**, 189 (1892)

widely adopted, the experimental evidence does not appear to exclude the possibility of electropy of the enol ion or radical nor of 1,4-addition (when conjugated systems are involved).

Although the conventional theory of addition to the double bond can be used to explain the abnormal behavior of benzylmagnesium chloride and its analogs, this theory does not satisfactorily account for the formation of 3-phenylpentene-1 (II) observed by Prévost.[11] In view of the comprehensive studies of Gilman and his collaborators,[16] it appears unlikely that the Grignard reagent can be assumed to add to the ethylenic bond in the system, $RCH{=}CHCH_2Br$.

The observation that products arising from the *o*-quinonoid structure are not observed in all reactions of benzylmagnesium chloride is our principal objection to accepting the hypothesis of Schmidlin and Garcia-Banùs as a complete elucidation of the mechanism of this transformation. The postulation of a rearrangement before the introduction of the reactant does not appear to suffice, since it does not account for the important effect of the nature of the reactant and does not allow a prediction of the result. It is obvious that certain structural features of the triad systems are prerequisite for the abnormal reaction, but the experimental evidence indicates clearly that the reactant must likewise possess some structural characteristic that is also requisite for the abnormal reaction. It would seem more reasonable to assume that the change of structure occurs in the course of the reaction, through rearrangement of electrons in a free benzyl radical or a benzyl ion.[17]

## Experimental

**Preparation of Grignard Reagents.**—All of the organomagnesium halides used in this study were prepared in the conventional manner; the few reactions that did not start spontaneously were initiated by the addition of a small quantity of ethylmagnesium bromide solution. The R—MgX content and the yields were determined by titration, using methyl red as indicator. Benzylmagnesium chloride was usually prepared in one mole runs, using one mole of halide to ten moles of ether. The yields were over 90% of the theoretical.

**Benzylmagnesium Chloride and Ethyl Chlorocarbonate.**—A repetition of the procedure used by Houben[5] led to the isolation of an ester fraction and a solid alcohol. In this experiment, as in other typical experiments, a solution of one equivalent of the organomagnesium halide was allowed to drop slowly into a well-cooled solution of slightly more than one equivalent of the reactant. The ester fraction proved to consist largely of ethyl *o*-toluate, as shown by saponification to *o*-toluic acid; m. p. 103–104°. This acid proved to be identical with *o*-toluic acid prepared from *o*-toluidine by way of *o*-tolunitrile.[18] A small amount of phenylacetic acid was present in the mother liquors. This result agrees with previous observations of Gilman.[6]

[16] Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928).

[17] A discussion of the application of electronics to isomeric change, with references to the original literature, is given by Stewart, Ref. 13, pp. 344–351. For references to the rearrangement of free radicals see Ref. 3(e).

[18] "Organic Syntheses," John Wiley and Co., Inc., New York, 1925, Vol. IV, p. 69.

The solid alcohol was recrystallized twice from ligroin, once from aqueous methyl alcohol and once from aqueous ethyl alcohol; m. p. 115–116°. The lower melting point, 108–111°, reported by Houben is probably due to the presence of dibenzyl as an impurity; Klages and Heilmann[19] report that tribenzylcarbinol melts at 114–115°. That this alcohol is the normal product, tribenzylcarbinol, was shown by its identity with the solid alcohol obtained by the action of benzylmagnesium chloride on ethyl phenylacetate, diethyl carbonate and dibenzyl ketone.[20] Since we were unable to obtain dibenzyl *o*-tolylcarbinol by the action of benzylmagnesium chloride on ethyl *o*-toluate, it seems unlikely that this carbinol is formed in the reaction between benzylmagnesium chloride and ethyl chlorocarbonate.

When benzylmagnesium chloride (3 moles) is added to an ethereal solution of ethyl chlorocarbonate (1 mole), the principal product is tribenzylcarbinol and only a very small amount of an ester fraction is obtained. It seems likely under these conditions that ethyl *o*-toluate is largely converted to benzyl *o*-tolyl ketone. Tribenzylcarbinol is also produced by the action of benzylmagnesium chloride on phenylacetyl chloride.

**Benzylmagnesium Chloride and Methyl Chlorocarbonate.**—The addition of 0.07 mole of benzylmagnesium chloride to an ice-cold solution of 10 g. of methyl chlorocarbonate in 25 cc. of ether gave an ester fraction from which 1.0 g. of *o*-toluic acid, m. p. 103–104°, was obtained. The melting point of this acid remained unchanged after mixture with an equal quantity of authentic *o*-toluic acid, m. p. 103–104°. An attempt to isolate phenylacetic acid from the reaction products was unsuccessful, but a microscopical examination[21] of the crude *o*-toluic acid showed the presence of some phenylacetic acid.

**Benzylmagnesium Chloride and Diethyl Carbonate.**—The principal product of this reaction is tribenzylcarbinol; after purification the crystals melted at 115–115.5°, and were identical with the specimens obtained by other methods. Only a trace of a low-boiling liquid fraction was obtained.

**Benzylmagnesium Chloride and Ethyl *o*-Toluate.**—Ethyl *o*-toluate was allowed to react with an excess of benzylmagnesium chloride, in an effort to prepare dibenzyl-*o*-tolylcarbinol. Although a reaction occurred, the desired alcohol could not be isolated. From 16 g. of ethyl *o*-toluate there was obtained 12 g. of a liquid, b. p. 225–227° at 7 mm., which was probably benzyl *o*-tolyl ketone. We did not succeed in identifying and characterizing this compound.

**Competition of Ethyl Phenylacetate and Ethyl *o*-Toluate for Benzylmagnesium Chloride.**—To a solution of 16 g. (0.1 mole) of ethyl phenylacetate and 16 g. (0.1 mole) of ethyl *o*-toluate in 100 cc. of dry ether, an ethereal solution of benzylmagnesium chloride (0.2 mole) was added slowly with stirring, during about four hours. The reaction mixture was decomposed with ice and diluted sulfuric acid and the ether layer separated. Ether extracts of the aqueous layer were combined with the original ether layer and dried over magnesium sulfate. After removal of the ether, there remained 46 g. of a liquid that yielded 15.5 g. of an ester fraction; b. p. 100–103° at 8 mm. Upon saponification this fraction gave 10 g. of crude *o*-toluic acid, m. p. 98–100°, which corresponds to a 72% recovery of ethyl *o*-toluate. The filtrates from the crystallization of the crude *o*-toluic acid were concentrated and yielded less than 1 g. of phenylacetic acid, which after crystallization from ligroin melted at 75–78°.

The residue from the distillation of the ester fraction solidified on cooling; the weight of this solid (21.5 g.), calculated as tribenzylcarbinol, represents a 71% conversion of the

[19] Klages and Heilmann, *Ber.*, **37**, 1456 (1904).

[20] Sachs and Loevy, *ibid.*, **36**, 1589 (1903).

[21] It was found that small amounts of either phenylacetic or *o*-toluic acid, in the presence of a large amount of the other, could be detected by this method.

ethyl phenylacetate. After recrystallization from alcohol, 8 g. of tribenzylcarbinol, m. p. 114–115°, was obtained. A mixed melting point with the tribenzylcarbinol prepared from benzylmagnesium chloride and ethyl chlorocarbonate was 115–116°.

**Benzylmagnesium Chloride and Carbon Dioxide (Solid).**—A solution of benzylmagnesium chloride (0.1 mole) was added to a slush of solid carbon dioxide and ether, with frequent shaking to avoid the formation of lumps. The reaction mixture was allowed to warm to 15° and was decomposed with dilute sulfuric acid in the customary manner. The crude acid weighed 5.4 g. (40% yield) and after crystallization from water melted at 76–77°. A mixed melting point with an authentic specimen of phenylacetic acid, prepared from benzyl cyanide, was 76–77°. Microscopical examination of all portions of the product indicated no trace of *o*-toluic acid.

***o*-Tolylmagnesium Bromide and Carbon Dioxide (Solid).**—The Grignard reagent was prepared in the usual manner from *o*-bromotoluene, in yields of over 90% of the theoretical. A solution of *o*-tolylmagnesium bromide (0.1 mole) was added to a slush of solid carbon dioxide and ether, as described above. There resulted 8.5 g. (62% yield) of crude acid, which after crystallization from ligroin and from water melted at 103–104°. A mixed melting point with an authentic specimen of *o*-toluic acid was 103–104°. All of the filtrates of precipitation and crystallization were evaporated and examined microscopically; no phenylacetic acid could be detected.

***o*-Tolylmagnesium Bromide and Dibenzyl Ketone.**—This reaction was carried out in an attempt to synthesize dibenzyl-*o*-tolylcarbinol. Dibenzyl ketone for this purpose was prepared in 65% yields by the distillation of calcium phenylacetate. A solution of *o*-tolylmagnesium bromide (0.17 mole) was added to 31 g. (0.15 mole) of dibenzyl ketone in 100 cc. of ether. The reaction mixture was treated in the usual manner and was subjected to steam distillation. The non-volatile portion was extracted with ether and gave 35 g. of an oil; on standing for five days a crystalline precipitate separated from this oil. The solid was separated by adding ligroin and filtering; from the filtrate 20 g. of unchanged dibenzyl ketone was recovered.

The crystalline solid was crystallized twice from alcohol and twice from acetone; it formed fine white needles which melted at 157–158° when heated rapidly, or at 154° in a slowly heated bath. Analyses[22] indicate that the compound is not dibenzyl-*o*-tolylcarbinol ($C_{22}H_{22}O$); its composition corresponds more closely to that of tetrabenzyl ethylene glycol ($C_{30}H_{30}O_2$).

*Anal.* Calcd. for $C_{22}H_{22}O$: C, 87.4; H, 7.4. For $C_{30}H_{30}O_2$: C, 85.3; H, 7.1. Found: C, 85.82; H, 6.83.

**Benzylmagnesium Chloride and Acetic Anhydride.**—A solution of benzylmagnesium chloride (0.55 mole) was added slowly, with stirring, to a solution of 100 g. (1.65 moles) of acetic anhydride in 100 cc. of ether. After working up the product in the usual way there was obtained 23 g. (30% yield) of a liquid, b. p. 205–230°, that proved to be 2-methylacetophenone. The remainder of the reaction product, which probably contained dibenzylmethylcarbinol, was not investigated. The structure of the ketone was established by oxidation with sodium hypobromite solution.[23] From 13.5 g. of the ketone there resulted 6 g. of an acid which, after crystallization from ligroin and from water, melted at 104–105°. A mixed melting point with an authentic specimen of *o*-toluic acid was 104°. No trace of phenylacetic acid was found in the oxidation products from this ketone.

[22] We are indebted to Dr. Wallace H. Carothers of the Experimental Station of E. I. du Pont de Nemours and Co., for these microanalyses. The values reported are the mean results of five concordant analyses.

[23] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 108.

**Benzylmagnesium Chloride and Chloroacetic Anhydride.**[24]—A solution of benzylmagnesium chloride (0.5 mole) was added slowly, during the course of two hours, to a well-stirred solution of 105 g. (0.6 mole) of chloroacetic anhydride in 600 cc. of ether at 0°. During the course of the reaction a white crystalline solid precipitated. The reaction mixture was decomposed with ice-cold dilute hydrochloric acid and the ether layer and extracts were dried over magnesium sulfate. On fractionating the product there was obtained 36 g. (42% yield) of a halogenated ketone, b. p. 125–135° at 14 mm., with strong lachrymatory properties. On redistillation there was obtained a clear pale yellow liquid, b. p. 129–130° at 11 mm., which proved to be chloromethyl *o*-tolyl ketone.

*Anal.* Calcd. for $C_9H_9OCl$: Cl, 21.04. Found: Cl, 20.90.

The semicarbazone of chloromethyl *o*-tolyl ketone was found to melt at 103–105°. The structure of the ketone was established by oxidation with sodium hypochlorite; 10 g. of the ketone gave 4.5 g. (56% yield) of *o*-toluic acid which melted at 104°. This was checked by a mixed melting point with an authentic specimen.

**Benzylmagnesium Chloride and Acetyl Chloride.**[8]—A solution of the Grignard reagent (0.37 mole) was added slowly to 39 g. (0.5 mole) of acetyl chloride in 400 cc. of ether. During the course of the reaction a white precipitate formed. The reaction mixture was treated in the usual manner and gave 12 g. (24% yield) of a ketone fraction boiling mainly at 102–103° at 22 mm., and 202–206° at 745 mm. This product proved to be almost entirely *o*-methylacetophenone, as shown by examination of the semicarbazone and by oxidation to *o*-toluic acid.

A sample of 1.5 g. of the ketone, on oxidation with sodium hypobromite solution gave 0.9 g. of crude *o*-toluic acid; after three crystallizations from water this acid melted at 102–103°, and a mixed melting point with authentic *o*-toluic acid was 103–104°.

The semicarbazone of the ketone melted at 202°; since the values 192°[25] and 203°[26] are reported in the literature, comparison was made with the semicarbazone of authentic *o*-methylacetophenone. For this purpose, the ketone was prepared by the action of methylmagnesium iodide on *o*-tolunitrile. The synthetic ketone boiled at 204° at 745 mm., and its semicarbazone melted at 205°. A mixed melting point of this semicarbazone with the one obtained above was 204–205°.

**Benzylmagnesium Chloride and Benzoyl Chloride.**—This reaction was first carried out by adding benzylmagnesium chloride to an excess of benzoyl chloride in ether, cooled in an ice–salt mixture. This procedure led to the formation of a relatively small amount of the ketone fraction and a large amount of the tertiary alcohol. Subsequently, it was found that the yield of the ketone fraction was increased by cooling the ethereal solution of benzoyl chloride in a bath of carbon dioxide snow.

A solution of benzylmagnesium chloride (0.24 mole) was added slowly, with vigorous stirring, to a solution of 70 g. (0.5 mole) of benzoyl chloride in 50 cc. of ether, cooled in carbon dioxide snow. The reaction mixture was decomposed with 30% sulfuric acid and subjected to steam distillation. The oily residue was taken up in ether, washed thoroughly with dilute alkali and dried. After removal of the ether, there remained 37 g. of a liquid which was fractionated under reduced pressure. A fraction collected at 162–184° at 11 mm., on redistillation gave 9 g. of a ketone which distilled almost completely at 164–169° at 9 mm., and proved to be phenyl *o*-tolyl ketone (2-methylbenzophenone). A sample of 1.4 g. of this ketone on oxidation with aqueous potassium

[24] This experiment was carried out by Mr. Tab Nilanidhi, in connection with a study of the preparation of chloromethyl ketones from various Grignard reagents and chloroacetic anhydride.

[25] Senderens, *Ann. chim. phys.*, [8] **28**, 330 (1913).

[26] Auwers, *Ann.*, **408**, 242 (1915).

permanganate solution gave 0.6 g. of an acid; the latter after several crystallizations from ligroin and absolute alcohol, melted at 127°. A mixed melting point with an authentic specimen of *o*-benzoylbenzoic acid, m. p. 127°, showed no depression.

Fractional distillation of the higher boiling material in the crude reaction product gave 10 g. of a liquid, distilling almost entirely at 224–235° at 8 mm., that solidified on cooling. This was recrystallized twice from ligroin, and from aqueous alcohol; m. p. 84–85°. This substance proved to be identical with a specimen of phenyldibenzylcarbinol, m. p. 84–85°, prepared from benzylmagnesium chloride and ethyl benzoate. Klages and Heilmann[19] reported 86–87° for the melting point of this carbinol.

### Reactions of 2-Chlorobenzylmagnesium Chloride

**Preparation of the Grignard Reagent.**—*o*-Chlorotoluene was chlorinated at the boiling point, in a quartz flask, in the light of a mercury vapor lamp; it was found advisable to underchlorinate slightly. The purified *o*-chlorobenzyl chloride had the following boiling points: 84–85° at 3 mm., 96–98° at 14 mm., 110° at 24 mm. The Grignard reagent was always prepared with the freshly distilled halide, using 10 moles of ether to one of the halide; the yields varied from 60–75% of the theoretical. Since this organomagnesium halide appeared to be particularly sensitive to atmospheric oxidation, it was prepared in small amounts and used at once.

***o*-Chlorobenzylmagnesium Chloride and Carbon Dioxide (Gas).**—This reaction produced *o*-chlorophenylacetic acid, which formed white needles melting at 94–95°. The melting point recorded for this acid in the literature[27] is 95°; the melting point of 2-methyl-3-chlorobenzoic acid is 159°.[28]

***o*-Chlorobenzylmagnesium Chloride and Methyl Chlorocarbonate.**—A solution of the Grignard reagent (0.032 mole) was added slowly to an excess of methyl chlorocarbonate in 50 cc. of ether, cooled to 0°. The crude reaction product containing the ester fraction was saponified by strong potassium hydroxide solution, and upon acidification gave 1 g. of an acid. After two crystallizations from alcohol and water, the acid melted at 95–96° (softening at 93°). A mixed melting point with *o*-chlorophenylacetic acid obtained in the preceding experiment was 95–96°. It appears that the abnormal reaction does not occur to any appreciable extent in this case.

***o*-Chlorobenzylmagnesium Chloride and Acetic Anhydride.**—A solution of the Grignard reagent (0.07 mole) was added slowly to an ethereal solution of 50 g. (0.83 mole) of acetic anhydride, cooled in an ice–salt bath. The mixture was decomposed in the usual way but no attempt was made to isolate the pure ketone, due to the small quantity available. Oxidation with sodium hypobromite solution, and repeated crystallization of the resulting acid gave 0.1 g. of 2-methyl-3-chlorobenzoic acid; m. p. 159–160°. The formation of this acid indicates that the original ketone was 2-methyl-3-chloroacetophenone.

***o*-Chlorobenzylmagnesium Chloride and Acetyl Chloride.**—A solution of the Grignard reagent (0.042 mole) was added to an ice-cooled solution of 12 g. of acetyl chloride in 50 cc. of ether. The procedure outlined in the preceding experiment gave 0.2 g. of crude 2-methyl-3-chlorobenzoic acid. After three crystallizations the acid melted at 160° (softening at 157°); a mixed melting point with the 2-methyl-3-chlorobenzoic acid from the previous experiment was 159–161°. This indicates the presence of 2-methyl-3-chloroacetophenone in the reaction products.

### Reactions of 2,6-Dichlorobenzylmagnesium Chloride

**2,6-Dichlorotoluene.**—This compound was prepared by an adaptation of a method

[27] Mehner, *J. prakt. Chem.*, [2] **62**, 556 (1900).

[28] Noelting, *Ber.*, **37**, 1025 (1904).

previously described;[29] *p*-toluene sulfonyl chloride was chlorinated and the sulfonic acid group was removed by hydrolysis. One mole of *p*-toluene sulfonyl chloride (190 g.) mixed with 11 g. of antimony pentachloride was chlorinated at 70–80°, in a 500-cc. flask provided with a mechanical stirrer and reflux condenser. The chlorination was stopped when the gain in weight attained 69 g.; this required four to five hours. The crude 2,6-dichlorotoluene-4-sulfonyl chloride was converted to the sodium salt of the sulfonic acid by pouring the reaction mixture carefully into a concentrated solution of sodium hydroxide. The sparingly soluble sodium 2,6-dichlorotoluene-4-sulfonate was recrystallized from water; the yields were 85–93% of the theoretical. Elimination of the sulfonic acid group was effected by heating with 85% sulfuric acid.

A mixture of 300 g. of the above salt and 1 liter of 85% sulfuric acid was refluxed for nine hours; 200 cc. of water was added and the solution was distilled until the aqueous layer of the distillate amounted to 250 cc. The reaction mixture was again refluxed for nine hours, 250 cc. of water was added, and the mixture was distilled until fumes started to appear (250–300 cc. of aqueous distillate had been collected). The heavy layer of 2,6-dichlorotoluene in the distillates was separated and dried over solid sodium hydroxide. The yield of crude product was 42–50% of the theoretical; the purified 2,6-dichlorotoluene boiled at 54–56° at 8 mm., $n_D^{20}$ 1.5510, $d_4^{20}$ 1.2686. A quantity of 2,3,6-trichlorotoluene (b. p. 96° at 10 mm., m. p. 41–42°) amounting to about 25% of the weight of 2,6-dichlorotoluene was isolated from the high-boiling fractions.

**2,6-Dichlorobenzyl Chloride.**—2,6-Dichlorotoluene was chlorinated in the manner described for the chlorination of *o*-chlorotoluene. The initial temperature was 194°, and the reaction was practically complete when the temperature reached 230°. The crude product was subjected to fractional distillation under reduced pressure; the main fraction, b. p. 107–110° at 9 mm., or 135° at 25 mm., consisted of a mixture of liquid and solid. After cooling thoroughly the solid was removed by filtration and was recrystallized twice from ligroin; m. p. 39–40°. The material can also be crystallized from alcohol and from ether; its lachrymatory properties make all crystallizations troublesome. For analysis, the 2,6-dichlorobenzyl chloride was recrystallized three times from ether, at the temperature of carbon dioxide snow, using the technique of Dufraisse.[30]

*Anal.* Calcd. for $C_7H_5Cl_3$:Cl, 54.45. Found: Cl, 54.18, 53.93.

The liquid material separated from the crystals appeared also to consist chiefly of 2,6-dichlorobenzyl chloride; its melting point was probably depressed by the presence of a small quantity of 2,6-dichlorotoluene. A dichlorobenzyl chloride has been described by Beilstein and Kuhlberg[31] but their product differs in physical properties from the one described above.

2,6-Dichlorobenzyl chloride is oxidized with difficulty to 2,6-dichlorobenzoic acid. Heating with dilute nitric acid[32] in a sealed tube at 140°, for twenty-four hours, produced an acid which, after recrystallization from water, melted at 136–137°; neut. equiv., 191.2. Oxidation with boiling aqueous potassium permanganate solution (fifteen hours) gave an acid, which was recrystallized twice from water and once from ligroin; m. p. 138–140°, neut. equiv. 191.4. The reported melting point of 2,6-dichlorobenzoic acid is 143.7°,[32] and the calculated neutralization equivalent is 190.9.

**Preparation of 2,6-Dichlorobenzylmagnesium Chloride.**—This preparation was carried out using 0.2 mole of the halide, 100 cc. of ether and slightly more than the theoretical quantity of magnesium turnings. The yields of RMgX were about 90% of the

[29] (a) Geigy and Co., German Patent, 210,856; *Friedländer*, **9**, 104 (1908–1910); (b) Davies, *J. Chem. Soc.*, **119**, 857 (1921).

[30] Dufraisse, *Ann. chim.*, [9] **17**, 133 (1922).

[31] Beilstein and Kuhlberg, *Ann.*, **146**, 317 (1868); **150**, 313 (1869).

[32] Cohen and Dakin, *J. Chem. Soc.*, **79**, 1111 (1901).

theoretical, when highly purified specimens of the halide were used. The yields were somewhat lower with less pure samples.

**2,6-Dichlorobenzylmagnesium Chloride and Carbon Dioxide (Gas).**—The acid obtained from 0.02 mole of the Grignard reagent after two crystallizations from dilute alcohol weighed 0.1 g.; m. p. 156–157° (softening at 150°). This acid is 2,6-dichlorophenylacetic acid and is identical with the acid obtained in the following experiment. Analyses and determinations of the neutralization equivalent are described below.

**2,6-Dichlorobenzylmagnesium Chloride and Methyl Chlorocarbonate.**—A solution of the Grignard reagent (0.047 mole) was added slowly to 10 g. of methyl chlorocarbonate in 25 cc. of ether. After decomposing in the usual way, the product was saponified with 30% potassium hydroxide solution. The alkaline solution was filtered from an unsaponifiable residue (see below) and gave 6 g. of a crude acid upon acidification. After three crystallizations from dilute alcohol the 2,6-dichlorophenylacetic acid melted at 157–158° (softening at 152°); neut. equiv.: calcd., 205.0; found, 206.5, 207.1.

*Anal.* Calcd. for $C_8H_6Cl_2O_2$: Cl, 34.60. Found: Cl, 34.83, 34.81.

A mixed melting point with the acid obtained from the reaction of carbon dioxide and 2,6-dichlorobenzylmagnesium chloride was 157–158° (softening at 152°). An attempt to oxidize this acid to 2,6-dichlorobenzoic acid, by means of aqueous potassium permanganate, was unsuccessful; the original acid was recovered unchanged.

The unsaponifiable residue separated from the alkaline solution of the acid crystallized from ethyl acetate in fine white needles, m. p. 165–166°. The molecular weight as determined by the depression of the melting point of camphor (Rast) was 339. This value indicates the presence of two dichlorobenzyl groups, and suggests the possibility that the compound may be 2,6,2′,6′-tetrachlorodibenzyl ketone (mol. wt. 348), or 2,6,2′,6′-tetrachlorodibenzyl. The quantity of material was insufficient for further investigation.

**2,6-Dichlorobenzylmagnesium Chloride and Acetic Anhydride.**—A solution of the Grignard reagent (0.056 mole) was added to a solution of 25 g. of acetic anhydride in 25 cc. of ether. After decomposition with dilute sulfuric acid and evaporation of the ether layer, an oily liquid remained. The crude product upon oxidation with sodium hypobromite solution gave an acid that was purified only with difficulty. After numerous precipitations and crystallization there was obtained 0.1 g. of a pure product, m. p. 157–158°, which proved to be identical with the 2,6-dichlorophenylacetic acid described above (mixed melting point, 157–158°). The formation of this acid indicates the presence of 2,6-dichlorophenylacetone in the reaction product.

**2,6-Dichlorobenzylmagnesium Chloride and Acetyl Chloride.**—The product of this reaction was oxidized with sodium hypobromite solution in the usual way. After repeated fractional precipitations and crystallizations there resulted about 0.1 g. of an acid, m. p. 188–189°, which was presumably 3,5-dichloro-4-methylbenzoic acid. Claus and Beysen[33] reported a melting point of 187–188° (uncorr.) for this acid. The isolation of 3,5-dichloro-4-methylbenzoic acid indicates the presence in the reaction product of 3,5-dichloro-4-methylacetophenone, a product of para rearrangement.

## Summary

Acetyl chloride, benzoyl chloride, acetic anhydride and chloroacetic anhydride have been found to react with benzylmagnesium chloride to produce *o*-tolyl ketones instead of the expected benzyl ketones.

The action of benzylmagnesium chloride on ethyl chlorocarbonate was found to give principally ethyl *o*-toluate and tribenzylcarbinol. It is

[33] Claus and Beysen, *Ann.*, **266**, 239 (1891).

suggested that the formation of these products depends upon a selective action of the Grignard reagent on the initial products of the reaction.

2-Chlorobenzylmagnesium chloride and 2,6-dichlorobenzylmagnesium chloride have been prepared and their behavior toward certain reactants has been investigated. The tendency of these reactants to yield products of rearrangement appears to decrease in the following order: acetyl chloride > acetic anhydride > methyl chlorocarbonate > carbon dioxide.

The mechanism of the rearrangement process in abnormal reactions of benzylmagnesium chloride is discussed.

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

# REDUCTION STUDIES OF SCHIFF BASES. I. THE REDUCTION OF METHYLENE-PARA-AMINOPHENOL AND ITS PROBABLE STRUCTURE

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Schiff bases of the simple type RCH=NR',[1] when of relatively high molecular weight, are apparently not polymerized, and can in many cases be hydrogenated to the corresponding secondary amines.[2] With bases obtained from aldehydes of low molecular weight, notably formaldehyde, polymerization occurs, and may be the cause of difficulties in reduction. Polymerization has been demonstrated for compounds such as methylene-aniline, methylene-toluidines, and ethylidine-aniline.[3] That a reversible relationship may exist among monomeric and polymeric forms was suggested by early investigators,[4] and was made to appear very probable by the work of Ingold and Piggott.[5] No account of the polymerization of these bases appears in the recent review by Carothers.[6]

Cyclic structures of the type (A) were assigned to certain polymeric

[1] These and the corresponding ketone derivatives may be called the azomethines: Möhlau, *Ber.*, **31**, 2250 (1898).

[2] See, *e. g.*, German Patent 211,869; Wheeler, THIS JOURNAL, **35**, 976 (1913); Shepard and Ticknor, *ibid.*, **38**, 381 (1916); Kaufmann and Müller, *Ber.*, **51**, 126 (1918); Skita and Keil, *ibid.*, **61**, 1452 (1928); Zechmeister and Truka, *ibid.*, **63**, 2883 (1930); Buck, THIS JOURNAL, **53**, 2192 (1931).

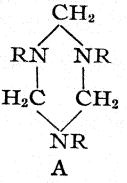
[3] Tollens, *Ber.*, **18**, 3309 (1885); Miller and Plöchl, *ibid.*, **25**, 2020 (1892); **29**, 1462 (1896); Pulvermacher, *ibid.*, **25**, 2762 (1892); Bischoff, *ibid.*, **31**, 3248 (1899).

[4] (a) Tollens, *ibid.*, **17**, 653 (1884), and Ref. 3; (b) Wellington and Tollens, *ibid.*, **18**, 3298 (1885).

[5] Ingold and Piggott, *J. Chem. Soc.*, (a) **121**, 2381, 2793 (1922); (b) **123**, 2745 (1923).

[6] Carothers, *Chem. Reviews*, **8**, 353–426 (1931).

Schiff bases by Bischoff,[3] Löb,[7] and Goecke,[8] on the basis of rather slight experimental evidence, though Miller and Plöchl[3,9] had pointed out the possibility of geometric isomerism for such compounds, and Bischoff[3] obtained two forms of methylene-*p*-toluidine which seemed to be so related, and whose existence was consistent with a ring structure. The study of the formation and thermal cleavage ("division") of certain compounds containing the 1,3-dimethinediazidine ring has in Ingold's laboratory yielded more substantial evidence for the ring structure of at least dimeric bases.[5,10] To a few dimeric bases Miller and Plöchl[3] and their students[11] were led by chemical evidence to assign somewhat doubtful open-chain formulas, *e. g.*, for ethylidine aniline: $C_6H_5N{=}CHCH_2CH(CH_3)NHC_6H_5$.



A

Reduction of Schiff bases has been used rather frequently as a method of alkylation, and occasionally to obtain indications as to their structure. Due to the present lack of definite information with respect to the course of aldehyde–amine condensations in acid media,[12] the results obtained by reduction can be interpreted in terms of structure probably only for Schiff bases formed in absence of acids.

Application of reduction to the problem of structure proof, as here proposed and exemplified below, involves these steps: (1) to show by molecular weight determinations that the Schiff base polymerizes, (2) to reduce the base strongly and identify and determine as completely as possible the products, and (3) to ascertain approximately the extent to which hydrolysis may interfere, so that formation of primary amine by reduction can be recognized if it occurs.

The results of a molecular weight determination may not be decisive, for the degree of polymerization may be determined in part by the solvent used, the temperature, etc. The influence of solvent is shown below in the case of methylene-*p*-aminophenol; that of temperature is inferable upon comparison of the results obtained for methylene-*p*-toluidine by Bischoff and later by Ingold and Piggott.[13] The determination of molecular weight,

[7] Löb, *Z. Elektrochem.*, **4,** 428 (1898).

[8] Goecke, *ibid.*, **9,** 470 (1903).

[9] Miller and Plöchl, *Ber.*, **27,** 1281 (1894).

[10] Ingold, *J. Chem. Soc.*, **125,** 87 (1924); **127,** 1141 (1925).

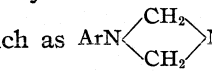
[11] Eibner, *Ber.*, **27,** 1296 (1894); *Ann.*, **318,** 58 (1901); **328,** 121 (1903); **329,** 210 (1903); Eibner and Purucker, *Ber.*, **33,** 3658 (1900); *cf.* Simon, *Ann. chim. phys.*, [7] **9,** 433 (1896); German Patents 376,013, 491,856.

[12] Though condensation in acid media has been variously reported to follow some special course, there seems to be in the literature evidence that the initial product, obtained in presence or absence of acid, is the simple azomethine, perhaps in hydrated form. A careful study of the course of condensation in acid media seems to be needed.

[13] Bischoff, *Ber.*, **31,** 3253 (1899); Ingold and Piggott, Ref. 5b. Bischoff found the compound to be trimeric in boiling benzene. Ingold and Piggott found it to be dimeric in freezing benzene, and monomeric at 250° (Victor Meyer method).

however, and especially if made in solvents indifferent with respect to association or the reverse, may at least show whether or not the base is capable of polymerization.

Reduction of Schiff bases is often complicated by hydrolysis, which is more pronounced with acid agents, and which regenerates the original amine and aldehyde.[4b,14] This may lead to secondary interference if the reduction is prolonged, for the regenerated aldehyde may condense with the hydrogenated base.[15] In order to minimize or avoid hydrolysis during reduction the most practical devices seem to be (1) to reduce in absence of water,[16] (2) to condense in presence of the reducing agent, *i. e.*, to reduce the nascent base,[17] or (3) to reduce the preformed base very rapidly, so that hydrolysis is put into disadvantageous competition with hydrogenation, as was done in the work described below.

The possible products of the reduction of a Schiff base will be determined by its structure. Simple azomethines ($RN{=}CHR'$) yield typically secondary amines. Alkylidene-diimines [$(RNH)_2CHR'$], which would yield primary and secondary amines, can be excluded from consideration if the amine and aldehyde condensed are of simple types,[18] and if excess of aldehyde is used.[14b] Compounds such as Bischoff's dimers, whose structure is doubtful, cannot well be considered in this connection, as their cleavage by reduction has not been reported. Cyclic polymerides, however, such as  , should yield as products of reduction *primary*, *secondary* and *tertiary* amines. To the reduction products named

[14] (a) O. Fischer, *Ber.*, **19,** 748 (1886); (b) Anselmino, *ibid.*, **41,** 621 (1908); (c) Skita and Keil[2]; (d) Langman, Healy and Dutt, *Quart. J. Indian Chem. Soc.*, **4,** 75 (1927); *Chem. Abstracts*, **21,** 2669 (1927); (e) Reddelien, *Ber.*, **48,** 1462 (1915); (f) Reddelien and Danilov, *ibid.*, **54,** 3132 (1921). Alkali is in some cases favorable to condensations: (g) Eberhardt and Welter, *ibid.*, **27,** 1804 (1894); (h) Bischoff and Reinfeld, *ibid.*, **36,** 41 (1903); (i) *cf.* Eibner, *ibid.*, **30,** 1444 (1897), and also (j) Wheeler and Smith, THIS JOURNAL, **41,** 1862 (1919).

[15] This perhaps accounts for the formation of a little dimethylaniline during the preparation of methylaniline by Frankland, Challenger and Nicholls [*J. Chem. Soc.*, **115,** 198 (1919)], using Morgan's method. The results of secondary condensations during acid reductions cannot well be predicted [*cf.* Goldschmidt, *Chem. Z.*, **24,** 284 (1900); **26,** 606 (1902); **28,** 1229 (1904); German Patent 96,851].

[16] O. Fischer, *Ber.*, **19,** 748 (1886); Mailhe, *Bull. soc. chim.*, **25,** 321 (1919); **27,** 229 (1920).

[17] Morgan, U. S. Patent 1,221,077; Skita and Keil.[2]

[18] Primary amines with negative substituents may condense to yield diimine bases: Pulvermacher;[3] Wheeler and Weller, THIS JOURNAL, **24,** 1063 (1902); Wheeler, *ibid.*, **30,** 163 (1908); Wheeler and Jordan, *ibid.*, **31,** 937 (1909); Jordan, *ibid.*, **32,** 973 (1910); Wheeler and Smith, *ibid.*, **41,** 1862 (1919); Kühling, *Ber.*, **27,** 567 (1894). Secondary amines yield typically the diimine bases: Braun, *ibid.*, **41,** 2145 (1908). Tertiary amines: Pinnov, *ibid.*, **27,** 3166 (1894); Möhlau and Heinze, *ibid.*, **35,** 359 (1902); Braun and Kruber, *ibid.*, **45,** 2991 (1912).

must be added any aldehyde and amine regenerated by hydrolysis. It may be concluded that the formation of primary amine (in quantity exceeding that attributable to hydrolysis), of secondary amine, and especially of tertiary amine, all as reduction products of a Schiff base known to polymerize, collectively constitutes evidence of a cyclic structure.

Formation of tertiary amine has been reported in only a few cases,[7,8,15,19] and then under circumstances which made the structural implications ambiguous. Primary amine has been obtained rather generally, but has apparently been regarded hitherto exclusively as an hydrolysis product. That primary, secondary and tertiary amines may all be formed as major products of the reduction of a Schiff base is shown below for the compound methylene-*p*-aminophenol. The structures of some other bases will be tested similarly in work now in progress.

**The Reduction of Methylene-*p*-aminophenol and its Structure.**—Methylene-*p*-aminophenol, produced by condensation of *p*-aminophenol and formaldehyde in alkaline[20] or neutral solution, is stated to be a polymeride,[21,22] though apparently without determination of its molecular weight. The view of Feldman[23] that it is only an addition product is incompatible with experimental results to be given below. No evidence as to the structure of methylene-*p*-aminophenol has been available hitherto.

The *molecular weight* of methylene-*p*-aminophenol was determined by the freezing point method in phenol and in trimethylcarbinol. Four specimens were examined, the averaged values in phenol being 147, 179, 127, 124 (calculated for monomer, 121),[24] while in trimethylcarbinol there was obtained the much higher value 408. These results suggest that methylene-*p*-aminophenol can exist wholly or largely monomeric and that it can polymerize, though more or less indefinitely, and that the molecular weight is not independent of the solvent.[25] It follows that the molecular

[19] German Patents 376,013, 491,856, 503,113.

[20] German Patent 68,707; *Frdl.*, Vol. 3, p. 996.

[21] Beilstein–Prager–Jacobson, "Organische Chemie," 4th ed., Vol. 13, p. 452.

[22] Levi, *Gazz. chim. ital.*, **59**, 544 (1929).

[23] Feldman, *Giorn. chim. ind. applicata*, **7**, 406 (1925); *Chem. Abstracts*, **20**, 3452 (1926).

[24] The first two specimens were made from pure *p*-aminophenol hydrochloride in alkaline solution saturated with hydrogen. The third was a specimen made from pure *p*-aminophenol in alkaline solution saturated with nitrogen; *Anal.:* nitrogen (Kjeldahl), 11.29%; calcd., 11.57%. The fourth value represents material made by neutral condensation: excess formaldehyde was added to a cold saturated solution of *p*-aminophenol, with air replaced by nitrogen, the product separating in crystalline form; nitrogen, 11.33%.

[25] It is possible that the high molecular weight in tertiary butyl alcohol was the result of association, though such solvents do not typically exert this influence [H. Meyer, "Analyse," 4th ed., J. Springer, Berlin, 1922, p. 417]. On the other hand depolymerization in phenol solution, while it has been observed for metacetaldehyde

weight in phenol or other solvent need not be that of the compound dissolved in acid for reduction. As appears below, the evidence of reduction indicates polymerization, perhaps by acid.[26] Experiments to test this for methylene-*p*-aminophenol were inconclusive.[27]

**Reduction of Methylene-*p*-aminophenol.**—Attempted reduction in alkaline media by various agents was not successful, as judged by absence of methyl-*p*-aminophenol separable as nitrosamine. Electrolytic reduction in acid solution,[28] using a lead cell of the type described by Lukens,[29] was in several trials partially effective, the best yield of methyl-*p*-aminophenol being 18%. Feldman[23] failed to hydrogenate methylene-*p*-aminophenol catalytically, but hydrogenation in alcohol and in presence of palladium has been claimed to give a good yield of secondary base.[30] Rapid and satisfactory reduction was effected by zinc dust and dilute sulfuric acid, both at about 20° and at higher temperatures.

To isolate the products of reduction, the liquid was made ammoniacal and extracted with ether in an automatic apparatus. During the extraction *p*-aminophenol crystallized from the ether in the boiling flask. As the methylated bases are freely soluble in ether, a useful and nearly complete separation of *p*-aminophenol present after reduction was thus very simply accomplished. The methylated bases were obtained from the ether extract by distillation under reduced pressure. They were weighed, dissolved in dilute acid, and in an aliquot part the secondary base was precipitated as nitrosamine and weighed. The dimethyl compound was either determined by difference, or was obtained from the nitrosamine filtrate, eventually by vacuum distillation. When necessary, *p*-aminophenol was identified as benzal-*p*-aminophenol (m. p. 185°, corr.); methyl-*p*-aminophenol as the nitrosamine (m. p. 135° corr.), or as the dibenzoyl derivative (m. p. 174° corr.); and dimethyl-*p*-aminophenol as the picrate (m. p. 170° corr.) or as the benzoate (m. p. 157–158°). Every isolation operation was separately examined as to accuracy, using weighed amounts of pure materials. The necessary corrections thus determined were relatively small, and are implicit in the results tabulated later.

In some of the reduction experiments it was possible to account for an average of 84% of the starting material in the form of recovered and identified products. As the work required for each complete experiment was somewhat prolonged, and involved a number of operations capable

[Hantzsch and Oechslin, *Ber.*, **40**, 4341 (1907)], would scarcely lead to different but reproducible values for different specimens of methylene-*p*-aminophenol.

[26] Law, *J. Chem. Soc.*, **101**, 154 (1912).

[27] Methylene-*p*-aminophenol recovered after treatment with acid showed increased molecular weight in phenol, but the material analyzed considerably too low for nitrogen.

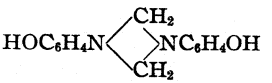
[28] *Cf.* German Patent 143,197.

[29] Lukens, *J. Ind. Eng. Chem.*, **13**, 562 (1921).

[30] German Patent 437,975.

of only moderate accuracy, it is not certain whether the 16% unaccounted for may be attributed to manipulative deficiency or to presence of some undetected reaction product. It was found that the reduction of methylene-*p*-aminophenol yielded methyl-*p*-aminophenol and dimethyl-*p*-aminophenol in about equal amounts, and that over 25% of the *p*-aminophenol originally condensed was regenerated. It was important to this inquiry to know whether this *p*-aminophenol was formed from methylene-*p*-aminophenol by hydrolysis wholly or by hydrolysis and reduction jointly. Experiments were made to determine approximately the extent of hydrolysis under the conditions of reduction but in absence of the reducing agents.[31] It was found that at about 20° the hydrolysis by 30% sulfuric acid was 9% in thirty minutes; and at about 80° it was 27% in fifteen minutes. While it seems improbable that hydrolysis was equally extensive when in competition with vigorous reduction, the results obtained for reduction below 25° make unnecessary any assumption on this point. In these reductions about 25% of the *p*-aminophenol was regenerated, of which not over about 10% (and probably less) was due to hydrolysis. It may therefore be stated that the reduction products of methylene-*p*-aminophenol were *p*-aminophenol, methyl-*p*-aminophenol, and dimethyl-*p*-aminophenol (see Table).

This result cannot be reconciled with the structure $HOC_6H_4N{=}CH_2$, nor with the view that polymers are molecular aggregates of this unit, except by assumption of secondary condensations (following hydrolysis) and secondary reductions, for which there is at present no useful evidence. As suggested in the introduction, the formation of primary, secondary and tertiary bases, all as reduction products of methylene-*p*-aminophenol, permits the conclusion that polymerized methylene-*p*-aminophenol is a valency compound with a structure analogous to that previously assigned to methyleneaniline and methylenetoluidine, and containing the type of hetero-elementary ring for whose existence in certain Schiff bases Ingold obtained experimental evidence of a different kind. For the simplest polymer this structure is

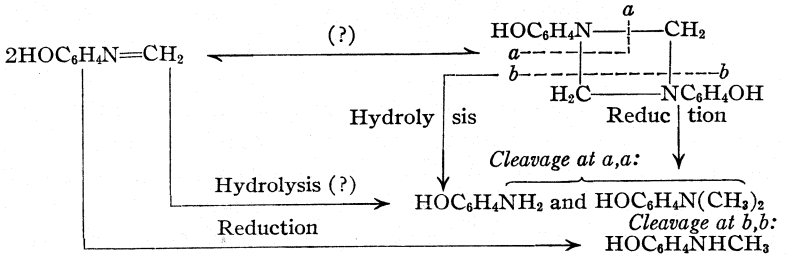


which, as well as higher polymers of like structure, could yield by reduction the products obtained.

The experimental facts, including the possibly labile relationship between monomer and polymers, the hydrolysis of both, and their reduction to

[31] The extent of the condensation was determined in an aliquot part, and the rest of the solution treated with acid. After suitable treatment to remove unhydrolyzed methylene-*p*-aminophenol (or its acid alteration product), the total *p*-aminophenol present was recovered and weighed as benzal-*p*-aminophenol.

the three bases obtained, may be presented diagrammatically as follows, using for simplicity the dimer:




## Experimental

### (1) Chemicals

*p*-**Aminophenol.**—For most of the work there was used the hydrochloride, purified by several crystallizations from hot approximately 6 *N* hydrochloric acid. *p*-Aminophenol base, used for preparation of pure methylene-*p*-aminophenol for analysis and molecular weight determination, was obtained from the pure hydrochloride, which was dissolved in water and the base precipitated by addition of saturated sodium sulfite solution. The product was crystallized from hot water, all the operations of recrystallization including the filtration being conducted with air replaced by nitrogen, and was dried *in vacuo*.

**Formaldehyde.**—There was used Baker's "C. P." solution, filtered, and assayed by the method of Romijn.

**Phenol.**—(1) A lot made from aniline was purified by distillation and by three partial freezings, the product melting at 41.2° corr. (2) Merck's phenol was distilled through a short packed column, the end fractions being discarded. The material boiled at 182.4° corr., and melted at 40.9° corr.

**Trimethylcarbinol.**—The Eastman product was purified by three partial freezings.

(2) **Apparatus.**—The outfit used in the condensation and reduction experiments was assembled in such manner as to permit all operations, up to the reduction itself, to be conducted in absence of air, which was excluded by flooding the entire closed system with nitrogen. The condensing vessel was an Erlenmeyer flask whose stopper carried two small separatory funnels, one for formaldehyde and the other for sodium hydroxide solution, as well as an inlet and an exit tube. Connections were so made that a single stream of nitrogen could be passed in series through all the liquids used before any of them were mixed. The precipitating apparatus consisted of a liter three-necked flask provided with a liquid-seal stirrer, a dropping funnel for dilute acetic acid, and a graduated separatory funnel for aliquotting. Sufficient water was put into the flask to afford suitable dilution of the condensation liquid before precipitating the methylene-*p*-aminophenol, and connections were so made that nitrogen from the exit tube of the condensing unit was passed in series through the graduated funnel, the water in the precipitation flask, and finally the acetic acid.

### (3) Procedure for Condensation and Reduction

**Condensation.**—In a typical experiment 25 g. of *p*-aminophenol hydrochloride was dissolved in 100 cc. of water in the condensing flask, 15 cc. of 36% formalin put into one separatory funnel and about 35 cc. of 40–50% sodium hydroxide solution into the other. The precipitation flask contained 250–300 cc. of water, and the acid funnel contained 6 *N* acetic acid. The whole system was flooded with nitrogen by passing

a rapid stream of the gas for about an hour. The condensation flask was immersed in an ice-bath, enough alkali solution was admitted to dissolve the aminophenol as phenolate, and after allowing the solution to cool the formaldehyde was added rapidly, and condensation allowed to proceed for two hours with chilling and with a slow stream of nitrogen passing. The entire liquid was then forced into the measuring funnel; to do this it was necessary to change one rubber tubing connection and to invert the condensing flask, when pressure of nitrogen effected the transfer. The flask was washed out with water saturated with nitrogen, the washings were transferred also, and the liquid in the measuring funnel was mixed.

To determine the extent of the condensation an aliquot part (*e. g.*, one-fifth) of the liquid was admitted to the precipitating flask. While operating the stirrer rapidly, dilute acetic acid was introduced by drops until precipitation was complete. The separated methylene-*p*-aminophenol was filtered, washed, dried *in vacuo* and weighed. To determine the *p*-aminophenol which escaped condensation, the slightly acid filtrate was shaken with a small excess of benzaldehyde, and the precipitated benzal-*p*-aminophenol[32] filtered off and weighed. The extent of condensation usually exceeded 80%; the highest yield recorded was 94%. The reaction was found to be not sensitive to changes in conditions, hence detailed data for numerous experimental condensations are omitted.

**Reduction.**—The measuring funnel, containing the main body of the condensation liquid, was withdrawn, the end of the stem passed below the surface of 60% sulfuric acid (a volume equal to that of the alkaline liquid) in a large beaker, and the solution was allowed to flow into the acid, the funnel being kept filled with nitrogen until it was empty and had been washed with water. Simultaneously with the introduction of the condensation liquid into the acid the addition of zinc dust was begun (a weight equal to that of the aminophenol salt), and was continued as rapidly as possible, the selected reduction temperature being maintained by cooling or heating, and the mixture mechanically stirred. Reduction was continued until nearly all the zinc had dissolved (about thirty minutes), but was probably complete long before this point was reached. Numerous experiments in which the conditions or the procedure were modified showed the reduction to be rather unresponsive to such changes.

(4) **Isolation of the Products of Reduction.**—The reduction liquid was poured into a mixture of chipped ice and strong ammonium hydroxide taken in moderate excess. The alkaline liquid was extracted with ether in a modified Schwarz "perforator."[33] After twelve to fifteen hours' extraction the *p*-aminophenol was filtered from the ether extract and weighed. The methylated bases were obtained from the ether solution by distillation under reduced pressure.[34] The mixed bases were weighed, and then dissolved in dilute sulfuric acid. An aliquot part of this solution was chilled in ice and treated with 25% sodium nitrite solution, and the precipitated nitrosamine was filtered off, washed sparingly with ice water, dried *in vacuo*, and weighed. In some experiments the dimethyl-*p*-aminophenol left in the nitrosamine filtrate was isolated finally by distillation under reduced pressure and weighed as base;[35] in others it was deter-

[32] Haegele, *Ber.*, **25**, 2753 (1892); German Patent 208,434.

[33] Houben, "Die Methoden der organischen Chemie," 3d ed., G. Thieme, Leipzig, Vol. I, 1925, p. 571. This useful apparatus was improved by introduction of a stirrer with liquid seal, and with paddles in the water and the ether layers opposed, so as to obtain a sliding interface.

[34] The boiling range of the mixture was about $157^{\circ}_{15}$ to $165^{\circ}_{18}$. A prepared mixture of about equal parts of monomethyl- and dimethyl-*p*-aminophenol boiled at $160^{\circ}_{18}$ to $162^{\circ}_{20}$.

[35] The yield of dimethylaminophenol thus found was decreased due to the fact that this compound is in some way reactive with nitrous acid, with evolution of gas.

mined by difference, its presence being shown by precipitation of the picrate. These methods of estimating the methylated bases were much better than the attempted separation of their sulfates, as used in earlier work.

The results of a number of complete experiments are presented in the table.

TABLE I

RESULTS FOR SOME EXPERIMENTS ON FORMATION OF METHYLENE-*p*-AMINOPHENOL IN ALKALINE SOLUTION, AND ITS REDUCTION BY ZINC DUST AND SULFURIC ACID

| Condensation | | | Reduction | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Yield,[a] % | Not condensed,[b] % | Total, % | Temp. of reduction, °C. | *p*-a. p. recovered after reduction, % | *p*-a. p. recov. *i* from hydr. and redn., % | Mixed methylated bases, % | Monomethyl *p*-a. p., % | Dimethyl-*p*-a. p., % | Total *p*-a. p., accd. for, % |
| 76.8[c] | 23.0 | 99.8 | 50–83 | 25.6 | 2.6 (?) | 33.8[e] | 24.4[f] | 16.8[e] | 66.8 |
| .. [c] | .. | ... | 45–88 | 35.9 | .. | 43.5[e] | .. | .. | 79.4 |
| .. [c] | .. | ... | 45–84 | 36.8 | .. | .. | 37.1[f] | .. | 73.9 |
| 85.8[d] | 16.3 | 102.1 | 60–80 | 20.2 | 3.9 (?) | .. | 18.4[e] | 20.6[e] | 60.1 |
| 76.8[d] | 21.4 | 98.2 | 80–85 | 26.0 | 4.6 (?) | .. | 23.6[f] | 22.5[g] | 74.8 |
| 88.8[d] | 15.5 | 104.3 | 70–90 | 26.1 | 10.6 | .. | 27.0[f] | 22.0[g] | 75.1 |
| 93.9[d] | 5.6 | 99.5 | 70–90 | 35.3 | 29.7 | 40.4[g] | 19.7[j] | 20.7[h,i] | 75.7 |
| .. [d] | 8.2 | ... | Below 25 | 35.5 | 27.3 | 56.3[g] | 30.8[f] | 25.7[h,i] | 92.0 |
| .. [d] | 13.7 | ... | Below 21 | 37.2 | 23.5 | 47.3[g] | 21.8[f] | 25.3[h] | 84.3 |
| Average of last three | 9.2 | | | 36.0 | 26.8 | 48.0 | 24.1 | 23.9 | 84.0 |

[a] Precipitated from an aliquot and weighed. [b] Precipitated and weighed as benzal-*p*-aminophenol. [c] Condensation at room temperature. [d] Condensation in ice-bath. [e] Separated and weighed as sulfate. [f] Separated and weighed as nitrosamine. [g] Isolated by distillation *in vacuo* and weighed as base. [h] Determined by difference. [i] Presence of dimethyl-*p*-aminophenol established by isolation of picrate. [j] Total *p*-aminophenol recovered after reduction minus that present due to failure to condense.

**(5) Methylene-*p*-aminophenol and Some Derived Compounds.**—Only a few observations believed to be new are appended.

**Methylene-*p*-aminophenol.**—Made in absence of alkali this compound was obtained as a crystalline precipitate. When made in presence of alkali and subsequently precipitated, it is an amorphous powder, practically white if made and isolated in an air-free system, but otherwise more or less discolored. In the air it darkens and finally becomes resinous. Methylene-*p*-aminophenol is insoluble in water, but dissolves in alkali (the solution darkens promptly in air), in ethyl and other alcohols, in phenol and aniline, and in dilute hydrochloric or sulfuric acid. The freshly prepared solution in acid appears to contain methylene-*p*-aminophenol, but on standing or heating some of the compound suffers hydrolysis, and some is rendered resinous and insoluble by secondary changes not yet explained. At present no method of purification is known, and no satisfactory test of purity is available, as the compound has not been found to be recrystallizable from any solvent tried, and has no determinable melting point. The specimens used for analysis and for molecular weight determinations were therefore prepared from pure materials and under such conditions that the isolated product would be as pure as possible.

**Dimethyl-*p*-aminophenol Picrate.**—This useful identifying derivative for the tertiary base has apparently not been reported hitherto. It was obtained by addition of sodium acetate to the slightly acid solution, and then an excess of saturated aqueous picric acid. On standing and chilling, the picrate separated as glistening yellow crys-

tals (sometimes discolored, and if obtained from the nitrosamine filtrate very dark in color). It was found to be identical (mixed melting point test) with the picrate obtained from Eastman dimethyl-*p*-aminophenol sulfate. After several crystallizations from hot water the compound melted at 167° uncorr. or 170.5° corr.

***p*-Hydroxyphenylmethylnitrosamine.**—This compound was mentioned by Clarke,[36] who gave the melting point as 136°, but it has not been carefully studied. The nitrosamine is the most satisfactory identifying derivative for methyl-*p*-aminophenol, its formation being a more characteristic (though less delicate) test than the color reaction with mercuric acetate described by Harger.[37] It can be crystallized from hot water containing a little alcohol (6 g. per 100 cc. of water with 10 cc. of alcohol added). When pure it is white, but it is difficult to obtain white if once discolored. The melting point of the compound three times recrystallized was 133.5° uncorr. or 135.5° corr. The nitrosamine is decomposed, with darkening, by strong acids and by hot strong alcohol. Reduction with zinc dust and hydrochloric acid in part regenerated the secondary base, 37% being recovered.

**Methyl-*p*-aminophenol.**—The boiling point of this base, apparently not reported, was found to be 168–169° (15 mm.) for a specimen isolated from the recrystallized sulfate (Eastman), and dried in ether solution over ignited sodium sulfate.

**Dibenzoyl-methyl-*p*-aminophenol.**—Methyl-*p*-aminophenol obtained in the reduction experiments gave by the Schotten–Baumann procedure a benzoyl compound melting at 174° corr. Clarke reported the dibenzoyl derivative to melt at 173°. As Reverdin[38] had obtained in presence of sodium acetate the monobenzoyl compound 4-(methylaminophenyl)-benzoate with the same melting point (173–174°), the derivative mentioned first was analyzed for nitrogen, the value 4.26% (Kjeldahl) establishing it as the dibenzoyl compound (calcd. N, 4.23).

## Summary

1. There is outlined for certain polymerized Schiff bases a method of structure proof based upon cleavage by reduction.

2. Experimental application of this method to the case of methylene-*p*-aminophenol showed that, following reduction by zinc dust and dilute sulfuric acid, up to 90% of the compound could be accounted for as *p*-aminophenol, methyl-*p*-aminophenol, and dimethyl-*p*-aminophenol produced by reduction, and *p*-aminophenol regenerated by hydrolysis. These findings permit the conclusion that polymerized methylene-*p*-aminophenol is a compound of cyclic structure containing the 1,3-dimethinediazidine ring, or a similar larger ring.

3. The ability of methylene-*p*-aminophenol to exist either in monomeric form or more or less polymerized was shown by determinations of molecular weight.

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[36] Clarke, *J. Ind. Eng. Chem.*, **10**, 893 (1918).

[37] Harger, THIS JOURNAL, **41**, 270 (1919).

[38] Reverdin, *Arch. sci. phys. nat.*, **27**, 383 (1909); *Chem. Abstracts*, **3**, 2139 (1909).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

# PARA-TOLUENE SULFONATES AS DERIVATIVES FOR THE IDENTIFICATION OF AROMATIC AMINES

BY C. R. NOLLER AND POE LIANG

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Forster and Keyworth have made a systematic investigation of the amine salts of benzene sulfonic acid,[1c] *m*-nitrobenzene sulfonic acid,[1d] *o*- and *p*-nitrotoluene sulfonic acids,[1e] $\alpha$- and $\beta$-naphthalene sulfonic acids,[1b] and the 2,6- and 2,7-naphthalene disulfonic acids,[1a] and have pointed out the advantages of these salts over other derivatives for identifying aromatic amines. Because of the ready availability of *p*-toluene sulfonic acid and the possibility that it might yield lower melting derivatives than any of the other sulfonic acids, we have prepared and determined the melting points of the *p*-toluene sulfonates of a number of the more common amino compounds. The results are summarized in the table.

On comparing our results with those of Forster and Keyworth, we find that the *p*-toluene sulfonates are in general lower melting than the previously described sulfonates with the exception of the $\alpha$-naphthalene sulfonates, where out of fifteen cases in which a comparison can be made, in eight cases the $\alpha$-naphthalene sulfonates are lower melting. The melting points of these compounds are listed in the table for comparison. The ready availability of *p*-toluene sulfonic acid would seem to give its use a slight advantage over $\alpha$-naphthalene sulfonic acid.

Three salts, namely, those of *p*-chloro- and *p*-bromoaniline, and *p*-aminobenzoic acid, were found difficult to prepare with a sharp melting point although analysis indicated them to be pure. In a number of cases great difficulty was found in causing the salts to crystallize and these have been reported as oils even though in a few cases the compounds have previously been isolated as solids. It was felt that if any special care was necessary in order to get crystalline products, the salt was not a satisfactory one for identification purposes. The failure to crystallize is the chief reason that the sulfonates are unsatisfactory derivatives for aliphatic amines.

Quite a few of the salts listed have been prepared before but in most such cases our preparations show a higher melting point. We have found that considerable care in drying the samples is necessary and traces of moisture may account for the lower melting points of other investigators. The previously recorded melting point and reference are also listed in the table.

[1] (a) Forster and Keyworth, *J. Soc. Chem. Ind.*, **43**, 165T (1924); (b) *ibid.*, **43**, 299T (1924); (c) Keyworth, *ibid.*, **43**, 341T (1924); (d) *ibid.*, **46**, 20T (1927); (e) *ibid.*, **46**, 397T (1927). References to other work on the sulfonates of amines will be found in these papers.

## TABLE I

### PARA-TOLUENE SULFONATES OF AMINES[a]

| Amine | Recryst. | Melting point, °C. Obs. | Corr. | Previously recorded m. p., °C. | Neut. equiv. Calcd. | Found | Nitrogen Calcd. | Found | M. p. of α-naphthalene sulfonate,[1b] °C. |
|---|---|---|---|---|---|---|---|---|---|
| Aniline | 2 | 232.0 | 238.4 | 223,[3] 235–235.5,[4] 230–231,[5] 216[6] | 265.2 | 265.4 | 5.28 | 5.31 | 183 |
| *o*-Toluidine | 2 | 185.5–186.2 | 189.7–190.5 | 180[3] | 279.2 | 278.0 | 5.02 | 4.97 | 237 |
| *m*-Toluidine | 2 | 171–172.5 | 174.6–176.1 | 161[7] | 279.2 | 277.4 | 5.02 | 5.00 | 195–196 |
| *p*-Toluidine | 3 | 193–194.5 | 197.7–199.2 | ... | 279.2 | 278.7 | 5.02 | 4.94 | 181 |
| 4-Amino-1,3-dimethylbenzene | 3 | 176.6–177.5 | 180.4–181.3 | ... | 293.2 | 291.7 | 4.78 | 4.71 | ... |
| *o*-Chloroaniline[b] | 3 | 188.5–189.2 | 192.9–193.6 | 198[6] | 299.6 | 297.0 | 4.67 | 4.47 | 237 |
| *m*-Chloroaniline[b] | 2 | 204.7–205.2 | 209.8–210.3 | ... | 299.6 | 299.1 | 4.67 | 4.56 | 176 |
| *p*-Chloroaniline[b] | 4 | 207–225 | 213–231 | 225–226[8] | 299.6 | 299.3 | 4.67 | 4.68 | 231 |
| *o*-Bromoaniline[b] | 2 | 201–201.5 | 206.1–206.6 | ... | 344.1 | 341.3 | 4.07 | 3.96 | ... |
| *m*-Bromoaniline[b] | 2 | 199.1–200 | 204.1–205.0 | ... | 344.1 | 344.0 | 4.07 | 3.99 | 168 |
| *p*-Bromoaniline[b] | 2 | 208–228 | 214.2–234.2 | ... | 344.1 | 343.9 | 4.07 | 4.05 | 224 |
| *o*-Nitroaniline | .. | Oil | ... | ... | ... | ... | ... | ... | ... |
| *m*-Nitroaniline | 2 | 208–209.5 | 213.5–215.0 | ... | 310.2 | 310.2 | 9.03 | 9.02 | 261 |
| *p*-Nitroaniline[c] | 2 | 226–228.5 | 232.2–234.7 | ... | 310.2 | 308.0 | 9.03 | 8.55 | 241 |
| *o*-Aminophenol[d] | 2 | 219–220.5 | 224.7–226.2 | ... | 281.2 | ... | 4.98 | 5.09 | ... |
| *m*-Aminophenol[d] | .. | Oil | ... | ... | ... | ... | ... | ... | 200 |
| *p*-Aminophenol[d] | 2 | 245–246.5 | 252.1–253.6 | 220–245(d.)[4] | 281.2 | 280.0 | 4.98 | 4.95 | ... |
| *o*-Aminobenzoic acid | 2 | 218.5–219.0 | 224.1–224.6 | ... | 154.6 | 154.7 | 4.52 | 4.57 | ... |
| *m*-Aminobenzoic acid | 3 | 248.4–249.0 | 255.9–256.5 | ... | 154.6 | 154.7 | 4.52 | 4.52 | ... |
| *p*-Aminobenzoic acid | 3 | 230–235 | 236.5–241.5 | ... | 154.6 | 156.7 | 4.52 | 4.52 | ... |
| *p*-Aminoacetophenone | 3 | 174–175.5 | 177.8–179.3 | ... | 307.2 | 314.1 | 4.55 | 4.50 | ... |
| α-Naphthylamine | 3 | 241.5–243.0 | 248.4–249.9 | 239[3] | 315.2 | 314.2 | 4.45 | 4.43 | 229 |
| β-Naphthylamine[b] | 3 | 212–213.8 | 217.3–219.1 | 219[9] | 315.2 | 317.8 | 4.45 | 4.45 | 200–201 |
| *o*-Aminodiphenyl[c] | 3 | 189.5–189.1 | 194.1–195.6 | ... | 341.2 | 340.8 | 4.11 | 4.20 | ... |
| *p*-Aminodiphenyl[b] | 2 | 246.5–247.6 | 253.8–254.9 | ... | 341.2 | 342.8 | 4.11 | 4.14 | ... |

TABLE I (*Concluded*)

| Amine | Recryst. | Melting point, °C. Obs. | Corr. | Previously recorded m. p., °C. | Neut. equiv. Calcd. | Found | Nitrogen Calcd. | Found | M. p. of naphthalene sulfonate,[1b] °C. |
|---|---|---|---|---|---|---|---|---|---|
| Benzylamine | 2 | 180.5–181.5 | 184.5–185.5 | 180[10] | 279.2 | ... | 5.02 | 5.04 | ... |
| Dibenzylamine | 2 | 155.5–156.5 | 158.3–159.3 | | 369.3 | 369.8 | 3.79 | 3.75 | ... |
| Tribenzylamine[c] | 2 | 200–202.5 | 205.2–207.7 | | 459.3 | 455.6 | 3.05 | 3.11 | ... |
| Benzylaniline | | 146–146.5 | 148.3–148.8 | | 355.2 | 356.0 | 3.94 | 3.94 | ... |
| Dibenzylaniline | | Oil | ... | | ... | ... | ... | ... | ... |
| *o*-Phenylenediamine | 2 | 259–260.5 | 267.3–268.8 | | 226.2 | 226.3 | 6.19 | 6.19 | ... |
| *m*-Phenylenediamine | 3 | 287–288 | 296.8–297.8 | | 226.2 | 226.4 | 6.19 | 6.27 | ... |
| *p*-Phenylenediamine | 3 | >340 | ... | | 226.2 | 226.4 | 6.19 | 6.10 | 330 |
| 2,4-Diaminotoluene | 3 | 262.5–263.0 | 270.8–271.3 | | 233.2 | 236.4 | 6.00 | 6.04 | ... |

[a] In addition to the salts listed in the table, unsuccessful attempts were made to prepare a number of others. Methylaniline, ethylaniline, dimethylaniline, diethylaniline, *p*-aminodimethylaniline, *i*-amylamine, di-*n*-propylamine, tri-*i*-amylamine, pyridine and quinoline gave oils which could not be readily crystallized. α- and β-aminoanthraquinone did not react with the sulfonic acid, or gave salts which were quite insoluble in water. [b] A large volume of water is necessary for recrystallizing the salts of β-naphthylamine, *p*-aminodiphenyl, *o*-chloroaniline, and *o*-bromoaniline. [c] A large excess of sulfonic acid must be used in preparing the salts of *o*-aminodiphenyl, *p*-nitroaniline, and tribenzylamine. Dilute hydrochloric acid (1 concd.:1 water) must be used in washing the salts of the last two compounds. [d] Benzylamine is too basic to titrate the *p*-toluene sulfonate, and the color of a solution of the salt of *o*-aminophenol is too deep to determine the end-point of the titration. [3] Norton and Otten, *Am. Chem. J.*, **10,** 140 (1888). [4] Bamberger and Rising, *Ber.*, **34,** 252 (1901). [5] Curtius and Kraemer, *J. prakt. Chem.*, [2] **125,** 323 (1930). [6] Heiduschka and Langkammerer, *ibid.*, [2] **88,** 425 (1913). [7] Meyer and Meyer, *ibid.*, [2] **68,** 290 (1903). [8] Halberkann, *Ber.*, **54,** 1833 (1921). [9] Slotta and Franks, *ibid.*, **63,** 678 (1930). [10] Neber and Uber, *Ann.*, **467,** 52 (1928).

## Experimental

Aqueous solutions of *p*-toluene sulfonic acid were prepared by refluxing a weighed quantity of *p*-toluene sulfonyl chloride, m. p. 64–66°, with distilled water until a homogeneous solution resulted. This was diluted with water to a volume such that the concentration of *p*-toluene sulfonic acid was 2.5 molar. No attempt was made to remove the hydrochloric acid formed on hydrolysis as it does not interfere with and, in some cases, even aids the formation of the amine sulfonate.

To form the salts, 20 cc. of the above solution was added to an equivalent amount of amine, *i. e.*, 0.05 mole of monoamines and 0.025 mole of diamines. The mixture was heated to boiling until a clear solution resulted, a small amount of decolorizing carbon added, the solution filtered hot and then cooled in an ice-bath. In some cases it was necessary to add more water while in others the solution had to be evaporated in order to get the optimum concentration for crystallization. The products were recrystallized to constant melting point. The salts were air dried or dried in a vacuum desiccator, and then dried at 110°.

The neutral equivalents were determined according to the procedure of Perkin and Sewell[2] using phenolphthalein as an indicator and heating to boiling toward the end of the titration. Nitrogen was determined by a modified Kjeldahl procedure.

## Summary

The *p*-toluene sulfonates of aromatic amines can, in general, be readily prepared in a pure state and are quite satisfactory derivatives for identification purposes.

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[2] Perkin and Sewell, *J. Soc. Chem. Ind.*, **42**, 27T (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

# THE DECOMPOSITION OF UNSYMMETRICAL MERCURI-ORGANIC COMPOUNDS: A METHOD OF ESTABLISHING THE RELATIVE DEGREE OF ELECTRONEGATIVITY OF ORGANIC RADICALS. II[1]

BY M. S. KHARASCH AND A. L. FLENNER[1]

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## Introduction

In previous publications of this series,[2] the view has been expressed that the terms "positive" and "negative" as applied to organic radicals are too indefinite to be of much use. The methods which have been used to establish the line of demarcation between the two classes of substituents are frequently unsatisfactory and sometimes even ambiguous;[3] hence contradictory results are obtained when these terms are employed. A single new term "relative electronegativity" has therefore been carefully defined with the intention of avoiding the difficulties apparently inherent in the use of the older nomenclature. That such an idea will prove to be adequate appears probable, since the users of the older terminology, when they speak of any particular pair of radicals, usually have in mind only the difference between the groups in question with respect to their attraction for electrons.

But the concept of relative electronegativity may be expected to go further and to yield results which are semi-quantitative. For example, the old classification placed phenyl, tolyl and *p*-chlorophenyl among the negative radicals, but failed to arrange them in any particular order. By use of the concept of relative electronegativity ordered series may be established, and the information thus obtained is of considerable importance in the interpretation and prediction of reactions involving the radicals in question.

In view of the large number of organic radicals, the task of arranging them in order might seem to be endless. It is hoped, however, that from data on radicals of certain important types, some broad generalizations may be drawn. The object of the work recorded in the present paper is to determine: (a) How the electronegativity of an aliphatic radical is affected by a lengthening of the carbon chain. (b) How the electro-

[1] The material presented in this paper formed part of a dissertation submitted in 1927 by A. L. Flenner to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the Ph.D. degree.

[2] Kharasch and Grafflin, THIS JOURNAL, **47**, 1948 (1925); *Science*, **58**, 1510 (1923); Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926).

[3] See chapter on "Negative Nature of Atomic Groups," by Henrich translated by Johnson and Hahn, John Wiley and Sons, Inc., New York, 1922.

negativity of the phenyl radical is affected by the introduction of various ortho, meta and para substituents.

**Validity of the Method for Determining Relative Electronegativity of Organic Radicals.**—The method of establishing the relative electronegativity of organic radicals has been described by Kharasch and Marker.[2] This method depends only upon the fact that when hydrogen chloride is added to an unsymmetrical mercury compound, the following reaction takes place.

$$R_1HgR + HCl \longrightarrow R_1H + ClHgR$$

The group $R_1$ which presumably first dissociates from the mercury and then combines with the hydrogen ion in solution to form the hydrocarbon $R_1H$ is defined as the more electronegative of the two radicals; that is, it has the greater attraction for electrons.

Data thus obtained have no validity whatever unless it can be shown beyond doubt that the mercurial used is really unsymmetrical. We have based our conclusions to this effect on the analysis of the substance in question and on the nature of its reactions with both hydrogen chloride and mercuric chloride. No results have been considered save in those cases where all lines of investigation led to concordant results. Certain investigators[4] have expressed the opinion, however, that, where analysis shows the presence of two different radicals, to obtain by the use of hydrogen chloride a single reaction product ($R_1H$) is not conclusive proof that the reacting substance is an unsymmetrical mercurial $R_1HgR$. This same result, they suggest, might be obtained from an equimolecular mixture of $R_1HgR_1$ and RHgR if the rate of reaction of the former compound were much greater than that of the latter compound. However, the decomposition by hydrogen chloride of an equimolecular mixture of mercury diethyl and mercury diphenyl has shown the objection to be unfounded. The mixture in question gives nearly equimolecular amounts of phenyl mercuric chloride and ethyl mercuric chloride in sharp contrast to the unsymmetrical phenyl mercury ethyl which yields ethyl mercuric chloride alone.

Furthermore, if the series of radicals obtained by this reaction is to find any sort of general applicability, it must be shown that the order of the groups is not usually affected by variations in any of the following factors: (1) the temperature at which the reaction is carried out; (2) the solvent used; (3) the concentration of the reaction mixture; (4) the relative solubility of the possible reaction products; (5) the purely hydrolytic agent used to accomplish the reaction; (6) the atom connecting the two organic radicals in question.

The effects of variations in temperature, concentration, solvent and hydrolytic agent used have been investigated by Kharasch and Pines[5]

[4] Private communication.

[5] Kharasch and Pines, unpublished work.

and within the range of their researches, no change in the order of the organic radicals has been found. Moreover, it has also been shown[2,5] that phenyl mercury ethyl, when dissolved in ether, is instantly decomposed by hydrogen chloride to form benzene and ethyl mercuric chloride in spite of the fact that phenyl mercuric chloride is much less soluble in ether than ethyl mercuric chloride, and hence would be the expected reaction product if relative solubility rather than relative electronegativity were the important influence guiding the course of the reaction. These results very nearly dispose of the criticisms of Wooster and Mitchell.[6]

In connection with the question as to the effect of variations in the hydrolytic agent used and the atom connecting the two organic radicals, the work and conclusions of Bullard[7] must be considered. Here it should be stated at once that since the arrangement of organic radicals in order of their relative electronegativity depends only upon the cleavage of the carbon to metal union it is best to employ a reagent which accomplishes selectively that type of reaction. As soon as reagents such as the halogens or mercuric salts are employed, a complication is introduced—that is, the possibility that the organic molecule may be attacked and altered before the cleavage occurs. For example, the reaction

$$R_2MCH_2R + Cl_2 \longrightarrow RMCl + ClCH_2R$$

[6] Wooster and Mitchell, THIS JOURNAL, **52**, 688 (1930). In our opinion, the other objections of Wooster and Mitchell may also be readily answered. These authors, after attempting to apply our hypothesis to triphenylmethane and similar hydrocarbons, state that the experimental facts are inconsistent with our views. The difference of opinion arises because Wooster and Mitchell make an assumption which seems to us of doubtful validity. They assume implicitly that when triphenylmethane and similar hydrocarbons react in liquid ammonia with alkali metals, the hydrocarbons ionize into a hydrogen ion and an organic ion, and that only the hydrogen ion reacts with the metal. Our view is that such reactions are reductions involving first the weakly electronegative carbon atom.

The ability to receive electrons is common to carbon atoms the valence electrons of which are shared with comparatively electronegative radicals and thus drawn into higher energy levels. When this occurs, hydrogen is not always the group eliminated in a subsequent splitting of the molecule. If a group less electronegative than hydrogen is present, it may be split off instead. For example, *sym.*-tetraphenylethane reacts with sodium–potassium alloy in dry benzene or ether to form potassium (sodium) diphenylmethyl [Ziegler and Thielmann, *Ber.*, **56B**, 1740 (1923)].

The idea that the hydrides of the most weakly electronegative radicals react most readily with metals is also supported by the behavior of the hydrides of carbon, silicon and germanium toward alkali metals, for the hydride of the most weakly electronegative element (germanium) is the one which reacts most readily with the metal.

In certain other arguments, Wooster and Mitchell have interpreted our theory peculiarly. Some of their predictions (*e. g.*, on the addition of bromine and sodium to phenylated unsaturated hydrocarbons) are contrary to the ones which we would make in the same instances. The facts, so far as we know, support our own predictions in all cases.

[7] Bullard, THIS JOURNAL, **51**, 3065 (1929).

might run directly as indicated. But on the other hand it might proceed in steps as

$$R_2MCH_2R + Cl_2 \longrightarrow R_1MCHClR + HCl$$
$$R_1MCHClR + HCl \longrightarrow R_1MCl + ClCH_2R$$

In this case it would not be the radical —$CH_2R$ but the radical —CHClR which was being cloven from the metal and consequently the reduction could throw no light on the position of the radical —$CH_2R$ in the table. In order to be sure what radical is being split off, it is necessary to use a cleavage agent which can react with the molecule in only one way; and among such agents are the acids which we have always employed.

Certain of Bullard's experiments with tetravalent tin derivatives, $R_3SnR_1$, probably suffered from complications of the kind indicated for some of them have been repeated[8] with the sole difference that halogen acids were used in place of chlorine, and in all cases the results have been found to be in agreement with our original table. Moreover, Kipping[9] has reported the splitting of tribenzylethylstannane by hydrochloric acid. He finds that the ethyl group is removed and tribenzyl tin chloride formed—a result in complete accord with our predictions.

Differences between the results obtained by the use of halogens and those obtained by the use of halogen acids would be expected to occur most strikingly when weakly electronegative radicals are involved. Thus Kraus and Bullard[10] have found that trimethylbenzylstannane and bromine yield trimethyl tin bromide and benzyl bromide

$$(CH_3)_3SnC_7H_7 + Br_2 \longrightarrow (CH_3)_3SnBr + BrC_7H_7$$

and Kipping and Smith[11] have reported that tribenzylethylstannane when treated with iodine gives dibenzyl ethyl tin iodide and benzyl iodide. On the basis of these and similar results Bullard[7] arrived at the order phenyl, benzyl, methyl, ethyl in contrast to our order phenyl, methyl, ethyl, benzyl. Whether by the use of halogens alone a self-consistent ordered series of radicals can be established seems rather doubtful in view of the complexity of the reactions involved. One thing, however, appears certain. If an ordered series can be thus obtained, it should not be expected to coincide at all points with the series obtained by the use of non-oxidizing cleavage agents.

Assuming that only purely hydrolytic agents are used, whether or not the order of relative electronegativity of organic radicals varies with the nature of the central atom becomes at once a clear cut and an important question. As far as we are aware, all known cases of the cleavage of unsymmetrical compounds support the table we have published. On

[8] Sher and Kharasch, unpublished work.

[9] Kipping, *J. Chem. Soc.*, 2366 (1928).

[10] Kraus and Bullard, THIS JOURNAL, **48**, 2135 (1926).

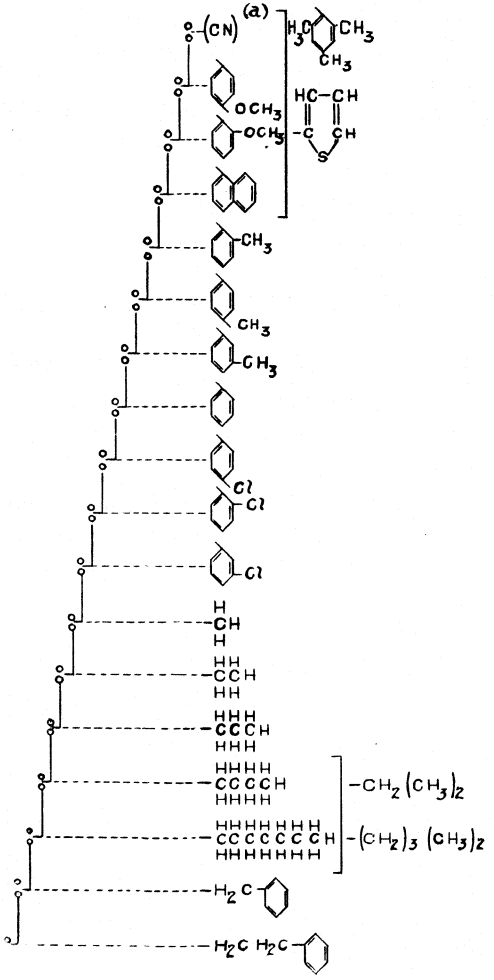
[11] Kipping and Smith, *J. Chem. Soc.*, **101**, 2553 (1912).

the other hand, our choice of the mercury organic compounds as a starting point was not a matter of chance.[12] It is desirable to use a metal (that is, a very weakly electronegative atom) so that the organic radical may readily capture the bonding electrons and split off at ordinary temperatures; and among organo-metallic compounds the unsymmetrical mercurials are peculiarly easy to isolate and identify. Moreover, when mercurials are used, since mercury is bivalent, it is unnecessary to consider questions of statistical probability such as might arise with a compound like RRRSnR.[2]

TABLE I

RELATIVE ORDER OF ELECTRONEGATIVITY OF ORGANIC RADICALS

The radicals to the right of the brackets have not been precisely placed as yet. It is known that they fall within the respective ranges indicated by the brackets.




(*a*) From silver cyanide.

**Arrangement of Radicals in the Order of Their Relative Electronegativity.**—The most important reaction of the unsymmetrical organo-mercuri molecules is their decomposition with hydrogen chloride. It should be emphasized once more that we consider the radical which dissociates more readily from the mercury and then combines with the hydrogen ion in solution to be the more electronegative of the two radicals. Using this criterion (and incidentally the results of Kharasch and Marker) the organic radicals studied are arranged in Table I. The compounds at the top of the table have a greater resemblance to the nonmetals while those below resemble the metals.

**Use of the Table of Relative Electronegativity of Radicals in the Interpretation of Organic Reactions.**—Although Table I is far from

[12] Kharasch and Reinmuth, *J. Chem. Ed.*, **5**, 407 (1928).

complete, it may be used in certain interesting ways to elucidate the properties of organic molecules. Some of these applications will be discussed briefly under the following heads: (1) the existence of free radicals, (2) the relative electronegativity of aliphatic radicals, (3) substitution reactions in the benzene ring.

(1) **The Existence of Free Radicals.**—The relation between the electronegativity of organic radicals and the degree of dissociation of the respective hexa-arylethane derivatives has been fully discussed by Kharasch and Marker. An hypothesis was presented for critical analysis rather than as a basis for any contention and conclusion.[13]

The failure of compounds such as dichlorotetraphenylethane to dissociate into free radicals (cited in refutation of our theory by Wooster and Mitchell)[6] was well known to us, but was not considered to be a discrepancy. We suggested that the dissociation of a hexa-substituted ethane would be promoted by any radical lying above phenyl in our Table of Relative Electronegativity. The well-established facts we believe are in harmony with our views. But since the positions of the halogens in the table have not yet been determined, it is premature to draw conclusions as to the dissociability of ethane derivatives loaded with halogens attached directly to the central carbon atoms.

The necessity for caution is illustrated by reference to Table I. The introduction of a chlorine atom into the benzene nucleus decreases the electronegativity of the radical no matter whether the entering chlorine be ortho, meta or para to the point of attachment. On the other hand, methyl and methoxy groups whether ortho, meta or para increase the electronegativity of the phenyl. Such facts are not readily inferred from a superficial examination of structural formulas; neither can they be obtained by simply applying the laws of electrostatic attraction. Moreover, it is an important (and in this case a very pertinent) fact that a molecule may relieve its internal stress in various ways other than by the formation of free radicals. Dissociation of the very labile halogen atoms in dichlorotetraphenylethane provides a second possible method of relief, and the decomposition of the molecule might take place in this manner. In conformity with our views, Schlenk and Racky[14] record that the halogens in dichlorotetrabiphenylethane are much more labile than those in di-

[13] Much attention has been paid to the substance prepared by Ziegler and Boye and called by them trinitrotriphenylmethyl [*Ann.*, **458**, 254 (1927)]. In view of the fact that these authors report neither the molecular weight of this compound nor the preparation of a peroxide from it, we cannot share their confidence that it is extensively dissociated. That a hexanitro compound should be strongly colored is scarcely surprising, and many substances for which dissociation into free radicals has not been suggested show when treated with bromine a rupture of the carbon to carbon bond. Ziegler and Boye's compound seems to us a questionable choice for a test case.

[14] Schlenk and Racky, *Ann.*, **394**, 211 (1912).

chlorotetraphenylethane, as regards both hydrolysis and liberation of chlorine.

Recently Ziegler and Mathes[15] have determined the dissociation constants of various para-substituted triphenylmethyl chlorides in liquid sulfur dioxide. Their results are in full agreement with the positions of these radicals in our table, and with the influence on the dissociation of the chloride ion which we have ascribed to them.

At this point it is necessary to call attention to another factor besides the relative electronegativity of radicals which very probably influences the course of reactions. In the valence bond R—X, if the radical X is joined to the organic radical through an atom of the elements B, C, N, O or F, then the valence electrons involved in the bond form part of the L shell of the elements in question. If the radical X is joined to the organic radical through an atom of Si, P, S or Cl, the valence electrons are part of the M shell. When the linkage is through Ge, As, Se or Br, the valence electrons are in the N shell, and when the linkage is through Sn, Sb, Te or I, they are in the O shell. In our opinion it is very doubtful whether linkages involving electrons from different shells can be directly compared with one another. A single ordered series containing radicals which involve linkages of the various sorts mentioned might very well prove misleading as a basis for the prediction of reactions.

Thus far, our own work on the electronegativity of organic radicals has involved only linkages through the carbon atom, and so the difficulty mentioned has not yet arisen for us. We have some confidence that the series we have begun can be extended to include linkages of metal to nitrogen, oxygen and fluorine; and similarly we hope that three other series involving, respectively, linkages to Si, P, S and Cl, to Ge, As, Se and Br and to Sn, Sb, Te and I may also be established. But whether, after these four series have been worked out, they can be usefully combined into a single series is a question which we wish to leave entirely open.

With regard to the halogens, in particular, great caution should be used. We believe that the fluorine atom can be included in the table containing carbon radicals and many of the properties of fluorine compounds are in harmony with this view. But the case of chlorine is quite different. It may well be that the stability of a bond involving electrons in the L shell differs widely from that of a bond involving electrons in the M shell, and if this is true, then in order to predict reactions where one of the radicals is a chlorine atom and another a carbon radical, a new factor (the shell of the valence electrons involved in the bond) in addition to relative electronegativity must be taken into account. (The same argument of course applies *a fortiori* to the halogens bromine and iodine.) For this reason we doubt the validity of arguments based on the behavior of such a compound

[15] Ziegler and Mathes, *Ann.*, **479**, 11 (1930).

as $\alpha,\beta$-dichlorotetraphenylethane. A far better substance for comparison would be $\alpha,\beta$-difluorotetraphenylethane and attempts to synthesize this compound are now under way.

**(2) The Relative Electronegativity of Aliphatic Radicals.**—As already stated by Kharasch and Marker,[2] if the radicals R and $R_1$ are widely separated in the Table of Relative Electronegativity, the decomposition of $R_1HgR$ proceeds quantitatively in one direction. If R and $R_1$ lie close together in the table, the decomposition with hydrogen chloride gives two products, but the substance containing the less electronegative radical always constitutes the greater proportion of the mixture of RHgCl and $R_1$-HgCl. In conformity with these views, we can report the following findings.

(*a*) Six repetitions of the cleavage of *n*-butyl mercury *n*-propyl showed the reaction product to consist of a mixture of 74.2 ± 1% of butyl mercuric chloride and 25.8 ± 1% of propyl mercuric chloride.

(*b*) Ethyl is much more strongly electronegative than *n*-heptyl for *n*-heptyl mercury ethyl is decomposed by hydrogen chloride to give nearly pure heptyl mercuric chloride and ethane.

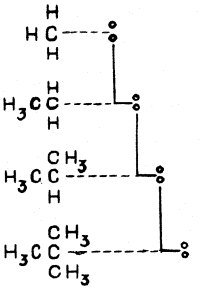
(*c*) The *n*-butyl radical however falls closer to *n*-heptyl, for *n*-butyl mercury *n*-heptyl gives a mixture of 70% of *n*-heptyl mercuric chloride and 30% of *n*-butyl mercuric chloride.

(*d*) By similar methods *n*-propyl has been shown to be more electronegative than isopropyl.

Judging by these data, the following conclusions appear to be justified: (1) In the straight chain aliphatic series, increase in the carbon chain leads to decrease in the electronegativity of the radical. No alternation in electronegativity has been observed. (2) Iso radicals are less electronegative than straight chain radicals and recent work with tertiary radicals indicates that their electronegativity is smaller still.

TABLE II

EFFECT OF SUBSTITUENT METHYLS ON THE ELECTRONEGATIVITY OF THE METHYL RADICAL



The order of arrangement is given in Table II.

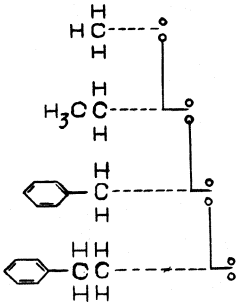
As to the effect of introducing a phenyl radical into an aliphatic chain, we can cite the following facts: (*a*) Kharasch and Marker[2] showed that ethyl is decidedly more electronegative than benzyl, for benzyl mercury ethyl is decomposed by hydrogen chloride to give 94% of benzyl mercuric chloride and 6% of ethyl mercuric chloride. (*b*) We now find that the $\beta$-phenylethyl radical is decidedly less electronegative than the benzyl radical, since the decomposition of benzyl mercury $\beta$-phenylethyl with

hydrogen chloride yields 10% of benzyl mercuric chloride and 90% of phenylethyl mercuric chloride.

Our conclusion is that the introduction of a phenyl group on the β-carbon atom of the ethyl radical must lower the electronegative character of that radical tremendously. That the *n*-butyl radical is more electronegative than the isobutyl radical appears to be in harmony with this view, but general conclusions must be postponed until further experimental work has been done. Table III summarizes the results so far obtained.

TABLE III

EFFECT OF A PHENYL GROUP ON THE ELECTRONEGATIVITY OF THE METHYL AND ETHYL RADICAL



**(3) Application of the Data on Relative Electronegativity to the Problem of Substitution in the Benzene Ring.**—No attempt will be made here to discuss the general merits and demerits of the various theories proposed to account for substitution in the benzene ring, since such a review would be beyond the scope of this article. It is our impression, however, that most of these theories have been built up *a posteriori* by inspecting the well-known data and then fitting the hypothesis to the facts. In contrast to such procedure, our treatment of the benzene substitution problem from the standpoint of relative electronegativity is based upon an experimental method which demands no knowledge of the position taken by an entering group when that group is substituted for one of the hydrogen atoms in a benzene derivative.

The data so far collected may be most conveniently treated by considering the following phases of the problem: (*a*) the effect of substituents on the electronegativity of the phenyl radical; (*b*) interpretation of the substitution reactions of aromatic substances in terms of the concept of electronegativity.

(*a*) Substituents introduced into the benzene ring may be divided into two classes according to whether they increase or decrease the electronegativity of the phenyl radical. The most remarkable feature of Table I is that when the substituents are thus divided, the methyl and methoxy radicals on the one hand, the chlorine atom[16] on the other hand, fall into different classes. All the tolyl and all the methoxyphenyl radicals are *more* electronegative than phenyl, while all the chlorophenyl radicals are *less* so. Yet all three of these substituents are ordinarily said to be nega-

[16] One of us and Pines (unpublished work) have extended this study to other (Br) halogen substituted phenyl radicals. The effect of this halogen on the electronegativity of the phenyl radical is quite similar to that observed with chlorine.

tive, and a close similarity between them is usually assumed on the ground that when attached to phenyl all three direct further substitution into the ortho and para positions. Clearly the classification of substituents according to their effect in raising or lowering the electronegativity of the phenyl radical leads to distinctions which are sharply at variance with current ideas.

If only a single substituent be considered, examination of Table I reveals the effect of altering the position of the group in question. Thus the lowering effect of the chlorine atom is greatest in the meta and least in the para position, from which it follows that the order of electronegativity of the three chlorophenyl radicals is $p > o > m$. It is perhaps worth noting that, so far as may be concluded from data now available, the effect of altering the position of a substituent seems to be much smaller than the effect of altering the substituent. For this reason the three radicals involving the same substituent occupy adjacent places in the table; no radical intervenes between the members of the different triads.

Considering first only those substituents which increase the electronegativity of the phenyl, certain interesting differences may be observed. The methyl radical exerts its maximum influence in the ortho position and gives the order $o > p > m$ for the tolyl radicals. The methoxyl radical on the other hand is most effective in the para position and gives for the methoxyphenyl radicals the order $p > o > m$. A finer subdivision of substituents into various sub-classes is thus indicated, but more data are needed before this idea can be developed.

Among the substituents which lower the electronegativity of phenyl, similar and even more striking differences may be noted. The radicals so far studied are —Cl, —Br, —$NO_2$ and —CN. Of these, the halogens have the greatest effect in lowering the electronegativity of the radical in the meta and a less effect in the ortho and para positions. Hence the order ($o$ and $p$) $> m$. But preliminary experiments on —CN indicate that with this substituent the order is reversed. The radical —CN has least lowering effect when it is in the meta position, which leads to the order of electronegativity $m >$ ($o$ and $p$).

The only conclusion which can at present be drawn from these curiously divergent effects is the necessity for great caution in making predictions.

(*b*) Independent of any particular mechanism of substitution in the benzene ring, it is evident from Table I that there is a relation between electronegativity and ease of substitution. Thus anisole, the hydride of the most electronegative radical investigated, is much more easily substituted than benzene, the hydride of the less electronegative phenyl radical. It is also well known that naphthalene and thiophene are much more reactive than benzene—facts which agree with the positions of their respective radicals in the table. Greater electronegativity, therefore, seems to imply a higher rate of reaction.

The first and most obvious application of this idea is to the triads of radicals containing a common single substituent. If the order of such a triad is ($o$ and $p$) > $m$, the substituent in question is an ortho–para directing group; if the order is $m$ > ($o$ and $p$), the substituent is meta directing.

This generalization moreover suggests that in competitive reactions a larger quantity of the substitution product of the more electronegative radical should be formed. Thus the positions of the chlorophenyl radicals in the table indicate that chlorobenzene should be less readily attacked by reagents than benzene, and that the products of substitution should be mainly para and ortho. The facts substantiate these predictions.[17] Similarly, since all the tolyl radicals lie above benzene in the table while all the chlorophenyl radicals lie below it, toluene should be attacked before chlorobenzene. This prediction accords with the observation of Wibaut,[18] who demonstrated that the velocity of nitration of toluene is greater than that of chlorobenzene.[19]

Another proposed rule which seems important may be drawn from the following facts. The substituents chlorine, bromine and the nitro radical may all be attached to the benzene ring by a process of direct substitution, and all of them lower the electronegativity of phenyl. Not a single group which can be thus directly introduced into benzene is to be found among those substituents which increase the electronegativity of phenyl. It would thus seem that *direct substitution by its very nature reduces the electronegativity of phenyl, and if this is the case all compounds formed from benzene by direct substitution will be less reactive toward new substituents than benzene itself.* The work of Kharasch and Legault[20] on mono and di-substituted phenyl radicals bears out this idea.

When two substituents both of which shift the electronegativity of phenyl in the same direction are introduced together into the benzene ring, it is reasonable to predict that the electronegativity of the resulting radical should be shifted even further from that of phenyl. For example, hydroxy and methyl radicals both increase the electronegativity of phenyl, and so the cresyls should be even more electronegative than the tolyl and hydroxy-

[17] Note the rather unsatisfactory reply of Holleman to the objections raised by Van der Linden relative to the difference in the speed of bromination of chlorobenzene and benzene [Holleman, "Some Factors Influencing Substitution in the Benzene Ring," *Chem. Reviews*, **1**, 195 (1924–1925)]. Van der Linden's objection is readily answered from the standpoint of difference in the relative electronegativity of the radicals.

[18] Wibaut, *Rec. trav. chim.*, **34**, 241 (1915).

[19] Holleman,[17] page 204, remarks with reference to these findings. "It was evident that toluene nitrated much more rapidly than chlorobenzene, just the reverse of what had been expected. This result was corroborated further by the nitration of chlorobenzene and of toluene separately in acetic anhydride solution."

[20] Kharasch and Legault, Master's dissertation, University of Maryland, unpublished work.

phenyl radicals; on the other hand, since both chlorine and the nitro groups decrease the electronegativity of phenyl, the chloronitrophenyls should be less electronegative than the chlorophenyl and nitrophenyl radicals. Furthermore, direct substitution should exert its lowering effect not only on phenyl but also on substituted phenyl radicals; for instance, the chlorotolyls should be less electronegative than the tolyl radicals.

In radicals such as the chlorotolyls, the effects of the two substituents are opposed and a complex interplay of forces results. Thus methyl increases the electronegativity of phenyl in the order $o > p > m$, while chlorine decreases the electronegativity and gives rise to the order $p > o > m$. Under these circumstances it is not surprising that Wibaut[21] when he nitrated orthochlorotoluene should have observed the formation of all four possible isomers.

Summing up, we believe we have shown that the idea of relative electronegativity distinguishes as effectively as other schemes between ortho–para and meta directing groups. In addition it accounts successfully for the lowered reactivity of the chlorinated and brominated benzenes. And finally it shows for the first time experimentally that the effect of methyl as a ring substituent is antagonistic to that of chlorine and hence that the ortho–para directing substituents are really of two distinct types. A quantitative measure of the effect of any given substituent in altering the electronegativity of the phenyl radical is, of course, still lacking, and therefore when various substitution products are formed at the same time, the ratios of the amounts produced cannot be exactly foretold. When the forces are very evenly balanced, secondary effects such as those of the solvent and of the temperature probably come into play, and may even in borderline cases alter the order of electronegativity of radicals which lie very close to one another in the Table. But in spite of such uncertainties, we believe that the concept of relative electronegativity throws more light on the problem of substitution in the benzene ring than any other theory now in the field.

## Experimental Part

**Method of Analysis for Mercury.**—A volumetric method of analysis for mercury is described by Rupp.[22] Koten and Adams[23] modified this method for the volumetric determination of mercury in organic compounds. In the Koten and Adams method a sample of the material is weighed into an Erlenmeyer flask and decomposed by a mixture of fuming nitric and sulfuric acids. Water is then added and a solution of potassium permanganate until a definite color persists. The excess of potassium permanganate is then destroyed by the addition of ferrous sulfate. Ferric alum is added as an indicator and the mercury titrated with potassium thiocyanate.

The above method is quite satisfactory for mercury compounds of the type $RHgR_1$,

[21] Wibaut, *Rec. trav. chim.*, **32**, 244 (1913).

[22] Rupp, *Chem.-Ztg.*, **32**, 1077 (1908).

[23] Koten and Adams, THIS JOURNAL, **46**, 2764 (1924).

but with any type of compounds containing halogen the method for obvious reasons fails absolutely.

After much experimentation the following volumetric method of analysis of mercuri-organic substances including those containing halogens was developed.

The procedure of analysis is as follows. About 0.2 g. of sample is weighed into a 250-cc. Erlenmeyer flask, 20 cc. of glacial acetic acid added and then 3 cc. of bromine. After standing for about twelve to twenty-four hours, 5 cc. of hydrochloric acid is added and then zinc dust, in small amounts at a time, care being taken to add the zinc slowly so that the temperature may not rise above 40°. As soon as all the color of bromine has disappeared, a slight excess of zinc is added and the mixture allowed to react for about two hours or longer. A small amount of finely powdered silica gel (the silica gel is added to retain any colloidal mercury that may be present) is then added to the mixture and the supernatant liquid filtered through a Gooch crucible, the asbestos pad of which has been previously covered with silica gel. The residue remaining in the flask is washed by decantation until free from halogen, the washings being poured through the Gooch crucible. The asbestos pad is then removed from the crucible and added to the residue in the flask and any mercury adhering on the walls of the crucible is washed into the flask by dilute nitric acid. The combined residue is dissolved in 1–1 nitric acid and when completely dissolved, the potassium permanganate, ferrous sulfate and ferric alum are added in the above order. The mercury is then titrated with potassium thiocyanate until the pink color persists.

It has been found important not to destroy the excess potassium permanganate with ferrous sulfate until just before the titration with potassium thiocyanate. Allowing the sample to stand with excess of potassium permanganate does not interfere with the analysis.

When titrating with potassium thiocyanate it was found necessary in order to insure the obtaining of the proper end-point that a blank be run and the colors made to check. Due to the tendency of the color to fade, this blank must be made just at the time of titration.

**The Decomposition of a Mixture of Mercury Diethyl and Mercury Diphenyl with Hydrogen Chloride.**—One gram of mercury diethyl was dissolved in 25 cc. of alcohol and 1.4 g. of mercury diphenyl added to it. Three cc. of alcohol saturated with hydrogen chloride was then added and the whole warmed to about 30° for two minutes. A precipitate separated. Water was then added and the solid collected on a filter. The solid was boiled with a small amount of alcohol and the residue collected on a filter. The melting point of the alcohol insoluble material was 248° and it was proved to be phenyl mercuric chloride. The weight was 1.10 g. Upon cooling the filtrate a product was obtained which melted at 185°. It was ethyl mercuric chloride mixed with a very small quantity of phenyl mercuric chloride. The weight of the ethyl mercuric chloride was 0.95 g.

**Preparation and Decomposition of Unsymmetrical Mercury Compounds.**—The method of preparation of the unsymmetrical organo-mercury compounds of Kharasch and Marker[2] was further modified. A complete description of the method follows.

About 8 g. of the organo-mercuri chloride is added in small portions at a time to about two molecular equivalents of the Grignard reagent of the other radical in anhydrous ether. The mixture is shaken constantly and kept immersed in ice water during the addition. After the addition of all the mercury compound the mixture is shaken until all of the solid has gone into solution.

$$R'HgCl + R''MgBr \longrightarrow R'HgR'' + MgBrCl$$

The excess Grignard reagent is then decomposed by ice and a 1% solution of sulfuric acid, care being taken that the temperature does not rise above 10°. The unsymmetrical

organo-mercuri compound is extracted with ether and dried with anhydrous sodium sulfate. It is then filtered, and the ether evaporated *in vacuo*, care being taken not to introduce any moisture. The product thus obtained is washed several times with anhydrous alcohol and dried *in vacuo*.

To about 1.2 g. of the above product, dissolved in ethyl ether, about 4 cc. of a saturated solution of hydrogen chloride in alcohol is added. The product is warmed slightly for about five minutes and the solution evaporated. The solid product obtained is then crystallized from a small amount of alcohol. The melting point of this compound is determined and mixed melting points taken with pure organo-mercuri chlorides of R′ and R″.

To another 1.2 g. of the unsymmetrical molecule in ether a molecular equivalent of mercuric chloride is added. The mixture is refluxed for about ten minutes, evaporated and the products separated and purified by the use of suitable solvents. The melting points of the products obtained are determined and the identity of the compounds further proved by taking mixed melting points with R′HgCl and R″HgCl. The following reaction takes place

$$R'HgR'' + HgCl_2 \longrightarrow R'HgCl + R''HgCl$$

A third portion of the unsymmetrical compound is dried to constant weight *in vacuo* and the percentage of mercury determined by the method described above.

The above procedure was carried out in a general way for each compound prepared and split, but certain modifications had to be made to suit the properties of the different compounds. One example will be given in detail while all others are listed in the summary, with footnotes giving any modifications.

**Preparation of Phenyl Mercury Phenylethyl,** $C_6H_5HgCH_2CH_2C_6H_5$.—Phenylethyl mercury chloride was first prepared by adding one molecular equivalent of mercuric chloride to phenylethylmagnesium bromide. The mixture was then decomposed by ice and 1% sulfuric acid and the compound isolated and purified. A small portion of this compound in alcohol was refluxed for about one hour with an excess of silver chloride in order to change any organo-mercuric bromide to the chloride. The pure compound was then isolated and the melting point determined, which was found to be 165°.

Five grams of phenyl mercury chloride was added to the Grignard reagent of phenylethyl bromide. After decomposition and purification a white crystalline compound was obtained which was found to have no definite melting point but which softened at 120° and melted slowly up to 170°.

*Anal.* Subs., 0.1500, 0.1909; 7.5, 9.5 cc. of KCNS (1 cc. = 0.01049 g. of Hg). Calcd. for $C_{14}H_{14}Hg$: Hg, 52.35. Found: Hg, 52.4, 52.2.

One gram of this compound was dissolved in alcohol and 0.71 g. of mercuric chloride added. On warming a heavy white precipitate formed which was collected on a filter. After several crystallizations from alcohol the insoluble portion melted at 250° and weighed 0.7 g. The melting point of the compound was not lowered by the addition of a small amount of pure phenyl mercury chloride, thus proving the substance to be phenyl mercury chloride.

The portion soluble in hot alcohol upon purification was found to have a melting point of 158° and weighed 0.8 g. The melting point of this product was not lowered by the addition of pure phenylethyl mercury chloride, thus proving the substance to be phenylethyl mercury chloride.

This shows that the unsymmetrical molecule was decomposed as follows

$$C_6H_5HgCH_2C_6H_5 + HgCl_2 \longrightarrow C_6H_5HgCl + C_6H_5CH_2CH_2HgCl$$

An additional one gram of the unsymmetrical compound was treated with an alcoholic solution of hydrogen chloride. Upon evaporation a white crystalline compound

## Summary of Experimental Work

The asterisk on a radical indicates that in the preparation of the unsymmetrical molecule the Grignard reagent of the radical so marked was treated with the organo mercury halogen derivative of the other radical, thus, $R_1{*}MgCl + RHgCl \longrightarrow R_1{*}HgR + MgCl_2$.

| Compound | M. p., °C. | Anal. of unsym. molecule: Subs., g. | Cc. of KCNS 1 cc. ≈ 0.01049 g. of Hg | Hg, % Found | Hg, % Calcd. | Decomp. unsym. molecules with $HgCl_2$ | Decomp. unsym. molecules with HCl |
|---|---|---|---|---|---|---|---|
| Phenyl mercury | 120–170 | 0.1500 | 7.50 | 52.45 | 52.20 | $C_6H_5HgCl$ + | M. p. 163°[b] $C_6H_5C_2H_4HgCl$ |
| *Phenyl ethyl | Dec. | .1909 | 9.50 | 52.35 | | $C_6H_5C_2H_4HgCl$ | |
| *Benzyl mercury | Liq. | .3657 | 17.50 | 50.20 | 50.56 | $C_6H_5CH_2HgCl$ + | M. p. 160°[a] $C_6H_5CH_2CH_2HgCl$ (90% ± 10%) + $C_6H_5CH_2HgCl$ (10% ± 10%) |
| Phenyl ethyl | | .3156 | 15.04 | 50.04 | | $C_6H_5C_2H_4HgCl$ | |
| Benzyl mercury | | | | | | | |
| *Phenyl ethyl | Liq. | .4167 | 19.85 | 49.96 | 50.56 | $C_6H_5CH_2HgCl$ + | Same |
| | | .3170 | 13.20 | 50.30 | | $C_6H_5C_2H_4HgCl$ | |
| Benzyl mercury | | | | | | | |
| *Phenyl ethyl | Liq. | | | | | $C_6H_5CH_2HgCl$ + | Same |
| | | | | | | $C_6H_5C_2H_4HgCl$ | |
| Thiophene | 80–120 | .2589 | 13.80 | 55.91 | 55.60 | $C_4H_3SHgCl$ + | M. p. 250° $C_6H_5HgCl$ |
| Mercury *phenyl | Dec. | .1907 | 10.10 | 55.56 | | $C_6H_5HgCl$ | |
| Heptyl mercury *ethyl | Liq. | .3420 | 19.85 | 60.88 | 61.02 | [b] | M. p. 120° $C_7H_{15}HgCl$ |
| *Heptyl mercury ethyl | Liq. | .3371 | 19.40 | 60.38 | 61.02 | [b] | M. p. 120° $C_7H_{15}HgCl$ |
| Heptyl mercury *butyl | Liq. | .3511 | 18.75 | 56.18 | 56.25 | [c] | M. p. 105°[d] $C_7H_{15}HgCl$ (70% ± 10%) $C_4H_9HgCl$ (30% ± 10%) |
| | | .3605 | 19.20 | 55.87 | | | |
| Isobutyl mercury *butyl | Liq. | .3140 | 19.00 | 63.43 | 63.80 | $C_4H_9HgCl$ + | M. p. 122°, main prod. (N)$C_4H_9HgCl$ |
| | | .3501 | 21.20 | 63.52 | | Iso-$C_4H_9HgCl$ | + small amounts of iso-$C_4H_9HgCl$ |
| Ethyl mercury | 188 | .2235 | 16.60 | 77.91 | 78.40 | | M. p. 193° $C_2H_5HgCl$ |
| Cyanide[e] | Dec. | .2608 | 19.25 | 77.42 | | | |
| *o*-Anisole | 175 | .2667 | 15.35 | 60.37 | 60.11 | | M. p. 179° $H_3COC_6H_4HgCl$ |
| Mercury cyanide[f] | Dec. | | | | | | |
| Isopropyl | Liq. | .4375 | 28.95 | 69.41 | 69.97 | (N)$C_3H_7HgCl$ + | M. p. 119° Iso-$C_3H_7HgCl$ (85% ± 10%) *n*-$C_3H_7HgCl$ (15% ± 10%) |
| Mercury *propyl | | .4082 | 26.95 | 69.25 | | Iso-$C_3H_7HgCl$ | |
| Phenyl mercury | 190–210 | .2231 | 10.70 | 50.31 | 51.55 | $C_6H_4ClHgCl$ + | M. p. 246°[g] *p*-$ClC_6H_4HgCl$ (80% ± 10%) $C_6H_5HgCl$ (20% ± 10%) |
| *p*-Chlorophenyl[h] | Dec. | .2099 | 10.10 | 50.47 | | $C_6H_5HgCl$ | |

SUMMARY OF EXPERIMENTAL WORK (*Continued*)

| Compound | M. p., °C. | Subs., g. | Anal. of unsym. molecule: Cc. of KCNS 1 cc. ≈ 0.01049 g. of Hg | Hg, % Found | Hg, % Calcd. | $HgCl_2$ | Decomp. unsym. molecules with HCl |
|---|---|---|---|---|---|---|---|
| *Phenyl mercury | 190–210 | 0.2581 | 12.35 | 50.19 | 51.55 | $C_6H_4ClHgCl$ | M. p. 246°.[g] *p*-$ClC_6H_4HgCl$ (70% ± 10%) + $C_6H_5HgCl$ (30% ± 10%) |
| *p*-Chlorophenyl[h] | Dec. | .2254 | 10.85 | 50.49 | | $C_6H_5HgCl$ | |
| Phenyl mercury | 190–210 | .2164 | 10.40 | 50.41 | 51.55 | $C_6H_4ClHgCl$ | M. p. 248°.[g] *p*-$ClC_6H_4HgCl$ (80% ± 10%) + $C_6H_5HgCl$ (20% ± 10%) |
| **p*-Chlorophenyl[h] | Dec. | .2907 | 14.05 | 50.66 | | $C_6H_5HgCl$ | |
| *Phenyl mercury | 90 | .2791 | 13.65 | 51.30 | 51.55 | $C_6H_4ClHgCl$ | M. p. 143°. *o*-$ClC_6H_4HgCl$ (95% ± 5%) + $C_6H_5HgCl$ (5% ± 5%) |
| *o*-Chlorophenyl | Dec. | | | | | $C_6H_5HgCl$ | |
| *Phenyl mercury | 89 | .2171 | 10.65 | 51.46 | 51.55 | $C_6H_4ClHgCl$ | M. p. 141°. *o*-$ClC_6H_4HgCl$ (90% ± 5%) + $C_6H_5HgCl$ (10% ± 5%) |
| *o*-Chlorophenyl | Dec. | .3756 | 18.45 | 51.53 | | $C_6H_5HgCl$ | |
| *Phenyl mercury | 68 | .2682 | 13.25 | 51.82 | 51.55 | $C_6H_4ClHgCl$ | M. p. 203°. *m*-$ClC_6H_4HgCl$ |
| *m*-Chlorophenyl | Dec. | | | | | $C_6H_5HgCl$ | |
| *o*-Chlorophenyl | 165–200 | .2137 | 9.55 | 46.88 | 47.36 | | M. p. 135°. Mostly *o*-$ClC_6H_4HgCl$ (70%+) |
| Mercury **p*-chlorophenyl | Dec. | .2419 | 11.00 | 47.70 | | | |
| *Phenyl mercury | 65 | .2175 | 11.10 | 53.53 | 54.42 | $C_6H_5HgCl$ + | M. p. 250°. $C_6H_5HgCl$ |
| *o*-Tolyl | Dec. | .4543 | 23.40 | 54.03 | | $CH_3C_6H_4HgCl$ | |
| **o*-Tolyl mercury | 195–205 | .2253 | 11.20 | 52.15 | 52.43 | *o*-$H_3CC_6H_4HgCl$ + | M. p. 228°. *p*-$H_3CC_6H_4HgCl$ (80% ± 10%) + *o*-$CH_3C_6H_4HgCl$ (10% ± 5%) |
| *p*-Tolyl | Dec. | .2104 | 10.50 | 52.35 | | *p*-$H_3C_6H_4HgCl$ | |
| *o*-Tolyl mercury | 200–210 | .2165 | 10.75 | 52.09 | 52.43 | *o*-$H_3CC_6H_4HgCl$ + | M. p. 230°. *p*-$H_3CC_6H_4HgCl$ (80% ± 10%) + *o*-$CH_3C_6H_4HgCl$ (20% ± 10%) |
| **p*-Tolyl | Dec. | | | | | *p*-$H_3CC_6H_4HgCl$ | |
| *o*-Tolyl mercury | 210–230 | .2218 | 10.40 | 49.18 | 49.76 | *o*-$H_3CC_6H_4HgCl$ + | M. p. 236°. *p*-$ClC_6H_4HgCl$ (95%) |
| **p*-Chlorophenyl | Dec. | .2106 | 10.00 | 49.81 | | *p*-$ClC_6H_4HgCl$ | |
| *o*-Tolyl mercury | 210–230 | .2207 | 10.40 | 49.42 | 49.76 | *o*-$H_3CC_6H_4HgCl$ + | M. p. 230°. *p*-$ClC_6H_4HgCl$ (95% ± 3%) |
| **p*-Chlorophenyl | Dec. | .3298 | 15.60 | 49.62 | | *p*-$ClC_6H_4HgCl$ | |
| *p*-Tolyl | 120–155 | .3686 | 19.10 | 54.35 | 54.41 | *p*-$H_3CC_6H_4HgCl$ + | M. p. 246°. $C_6H_5HgCl$ (90% ± 10%) + *p*-$CH_3C_6H_4HgCl$ (10% ± 5%) |
| Mercury *phenyl | Dec. | | | | | $C_6H_5HgCl$ | |
| *m*-Tolyl | 65–70 | .2235 | 11.50 | 53.97 | 54.41 | *m*-$H_3CC_6H_4HgCl$ + | M. p. 250°. $C_6H_5HgCl$ (80% ± 10%) + *m*-$CH_3C_6H_4HgCl$ (20% ± 10%) |
| Mercury *phenyl[i] | Dec. | .2022 | 10.40 | 53.95 | | $C_6H_5HgCl$ | |

SUMMARY OF EXPERIMENTAL WORK (*Concluded*)

| Compound | M. p., °C. | Subs., g. | Anal. of unsym. molecule: Cc. of KCNS 1 cc. = 0.01049 g. of Hg | Hg, % Found | Hg, % Calcd. | Decomp. unsym. molecules with $HgCl_2$ | Decomp. unsym. molecules with HCl |
|---|---|---|---|---|---|---|---|
| *m*-Tolyl mercury | 180–205 | 0.2036 | 10.20 | 52.55 | 52.43 | *m*-$H_3CC_6H_4HgCl$ + | M. p. 155°. *m*-$H_3CC_6H_4HgCl$ (90% ± 10%) + *p*-$CH_3C_6H_4HgCl$ (10% ± 10%) |
| **p*-Tolyl | Dec. | .2315 | 11.50 | 52.11 | | *p*-$H_3CC_6H_4HgCl$ | |
| *m*-Chlorophenyl | 95–100 | .2276 | 10.20 | 47.01 | 47.36 | *o*-$ClC_6H_4HgCl$ + | M. p. 207°. *m*-$ClC_6H_4HgCl$ (80% ± 10%) + *o*-$ClC_6H_4HgCl$ (20% ± 10%) |
| Mercury **o*-chlorophenyl | Dec. | .2113 | 9.55 | 47.40 | | *m*-$ClC_6H_4HgCl$ | |
| *m*-Tolyl mercury | 165–220 | .2125 | 10.10 | 49.86 | 49.76 | *m*-$H_3CC_6H_4HgCl$ | M. p. 230°. *p*-$ClC_6H_4HgCl$ (90% ± 10%) + *m*-$CH_3C_6H_4HgCl$(10% ± 10%) |
| **p*-Chlorophenyl | Dec. | .2161 | 10.20 | 49.51 | | *p*-$ClC_6H_4HgCl$ | |
| *o*-Tolyl mercury | Liq. | .2301 | 11.00 | 50.15 | 50.31 | [k] | M. p. 143°. *o*-$H_3CC_6H_4HgCl$ |
| **o*-Anisole | | .2355 | 11.20 | 49.89 | | | |
| Methyl mercury | Liq. | .2143 | 12.00 | 58.86 | 58.82 | $H_3CHgCl$ | M. p. 168°. $H_3CHgCl$ |
| **m*-Chlorophenyl | | .2285 | 12.70 | 58.29 | | *m*-$ClC_6H_4HgCl$ | |
| *p*-Anisole | 102 | .2353 | 10.75 | 47.92 | 48.40 | *o*-$H_3COC_6H_4HgCl$ | M. p. 175°. *o*-$H_3COC_6H_4HgCl$ |
| Mercury **o*-anisole | Dec. | .2287 | 10.50 | 48.15 | | *p*-$H_3COC_6H_4HgCl$ | |
| α-Naphthyl | 130–150 | .2076 | 9.10 | 45.98 | 46.15 | $C_{10}H_7HgCl$ | M. p. 183°. $C_{10}H_7HgCl$[l] |
| Mercury **p*-anisole | Dec. | .2256 | 9.95 | 46.27 | | *p*-$H_3COC_6H_4HgCl$ | |
| α-Naphthyl | 200–220 | | | | | | M. p. 188°. $C_{10}H_7gCl$[m] |
| Mercury **o*-anisole | Dec. | | | | | | |

[a] The separation of the two compounds was attained by fractional crystallization from alcohol. The amount of each component was determined by weight and the identity was confirmed by the fact that neither of them lowered the melting point of the corresponding pure material.

[b] The entire product resulting from the decomposition with mercuric chloride melted at 125°. It was found impossible to make any separation of the two compounds. An equal mixture of heptyl mercury chloride and ethyl mercury was prepared and this melted at 125° and was likewise found to be impossible to separate. The fact that the same result was obtained by preparing the compound in one case by using the Grignard reagent of the ethyl and in the other case the Grignard reagent of the heptyl offers sufficient evidence that the unsymmetrical compound was obtained. It will be noted that in each case the compound gave the correct analysis.

[c] The melting point of the decomposition product with mercuric chloride was 110° and it was found impossible to make any separation of products.

[d] The melting point of the decomposition product of the unsymmetrical molecule, heptyl mercury butyl, with hydrogen chloride indicates a mixture of the two mercury chlorides. The product was dried in a vacuum over sulfuric acid and analyzed. *Anal.* Subs., 0.2069, 0.2399: 12.55, 14.20 cc. of KCNS (1 cc. = 0.01049 g. Hg). Found: Hg, 62.5, 62.25. Since butyl mercury chloride contains 68.45% of mercury, and heptyl mercury chloride contains 50.8% of mercury, the mixture above contains 29.9 ± 1.0% of butyl mercury chloride and 70.1 ± 1.0% of heptyl mercury chloride.

[e] Ethyl mercury cyanide was prepared by refluxing one mole of ethyl mercury chloride with one and one-half moles of silver cyanide in benzene for one hour. The solution was then filtered and the benzene evaporated, leaving a white crystalline product which was crystallized from alcohol in white flakes. This last product gave no test for halogen.

[f] *o*-Anisole mercury cyanide was prepared similarly to ethyl mercury cyanide. After purification this product gave no test for halogen but after decomposition with hydrogen chloride and purification, gave a strong test for halogen.

[g] The percentage composition of the two components was estimated by analysis for mercury of the substance which resulted from the decomposition of the unsymmetrical molecule with hydrogen chloride. The results consistently indicated that about 80% of the solid was *p*-chlorophenyl mercury chloride. In view of the fact that a very small error in the mercury analysis affects appreciably the percentage composition of the solid, we have indicated what in our estimation constitutes the maximum error in the determination of the composition of the sample. (The authors are indebted to Mr. Pines for many of these analyses.)

[h] The unsymmetrical molecule phenyl mercury *p*-chlorophenyl was washed numerous times with petroleum ether but it was found difficult to obtain it in an absolutely pure state. It always retained a slightly brown color.

[i] The product obtained from the decomposition of *o*-chlorophenyl mercury *p*-chlorophenyl with mercuric chloride melted at 150 to 180°, indicating a mixture of the *o*- and *p*-chlorophenyl mercury chlorides, but all attempts to separate the two products failed. Equal mixtures of *o*-chlorophenyl mercury chloride and *p*-chlorophenyl mercury chloride melted at 150 to 180° and likewise gave the same difficulty in separation.

[j] The unsymmetrical molecule, *m*-tolyl mercury phenyl when first isolated was an oil which on treatment with petroleum ether in the cold immediately changed to a crystalline product. This compound was much more soluble in ethyl ether than the corresponding para compound.

[k] The product resulting from the decomposition of *o*-tolyl mercury *o*-anisole melted at 145°, which is similar to a mixture of *o*-tolyl mercury chloride and *o*-anisole mercury chloride. All attempts to separate these two products failed.

[l] The unsymmetrical compound α-naphthyl mercury *p*-anisole, being but slightly soluble in alcohol and ether and soluble in chloroform, it was thought best to decompose this molecule with hydrogen chloride in chloroform solution; 1.2 g., therefore, was treated with hydrogen chloride in chloroform. The solution was evaporated to dryness and the white residue dissolved in alcohol. Water was then added to the alcohol solution, forming a heavy white precipitate which was filtered and dried. The melting point of this product was found to be 80°, the melting point of naphthalene. This product also gave a strong odor of naphthalene. It is probable that the α-naphthyl mercury chloride was first formed and that this product was reacted upon by the excess hydrogen chloride forming naphthalene and mercuric chloride. An additional 1.2 g. of the unsymmetrical compound was then treated with hydrogen chloride in alcohol solution and after warming for about three minutes water was added, forming a heavy white precipitate which melted at 153°. The product melting at 153° was treated

with a small amount of hot alcohol, filtered and washed with a little cold alcohol. The residue gave a melting point of 183°. The weight of this product was 0.6 g. and its identity was confirmed by the fact that the melting point of the material was not depressed by admixture with pure α-naphthyl mercury chloride. With pure *p*-anisole mercury chloride the melting point was lowered to 161°.

To the alcohol filtrate and washings of the above, water was added and the precipitate which formed was filtered. The melting point of this product, about 0.1 g., was 80°, which is the melting point of naphthalene.

[m] The decomposition of naphthyl mercury *o*-anisole by hydrogen chloride was run in alcohol solution and gave results similar to naphthyl mercury *p*-anisole, naphthalene and naphthyl mercury chloride being formed.

was obtained which upon crystallization from alcohol melted at 160° and weighed 0.8 g. The melting point of this compound was not lowered by the addition of pure phenylethyl mercury chloride but when mixed with phenyl mercury chloride was lowered to 145°, thus proving the compound to be phenylethyl mercury chloride. This shows that the unsymmetrical molecule was decomposed as follows

$$C_6H_5HgCH_2CH_2C_6H_5 + HCl \longrightarrow C_6H_6 + C_6H_5CH_2CH_2HgCl$$

Upon repeating the above experiment a compound melting at 161° was obtained by treating the unsymmetrical molecule with hydrogen chloride and compounds melting at 250 and 165° were obtained on treatment with mercuric chloride.

The general method described with one specific example in detail gives an idea of the procedure employed in the experimental work, a summary of which follows. Any modification of the method is noted in footnotes under the designating symbol.

In each case all decomposition products isolated were weighed and no results considered unless quantitative yields were obtained.

The authors wish to acknowledge their indebtedness to Dr. James K. Senior for much help in connection with the preparation of this manuscript.

## Summary

1. The validity of the method of establishing experimentally the relative electronegativity of organic radicals is discussed.

2. An enlarged table of the order of electronegativity of organic radicals is given.

3. The Table of Electronegativity of Organic Radicals is employed in the study of the following topics: (*a*) the interpretation of the existence of free radicals; (*b*) the study of the effect of various substituents upon the electronegativity of the phenyl radical; (*c*) the study of substitution in the benzene ring.

4. The preparation and properties of a number of unsymmetrical organo-mercuri compounds are described.

5. A method is given for the analysis of compounds of the type RHgCl.

6. Various criticisms of the writers' views are shown to be untenable.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# PENTOSE REACTIONS. II. DERIVATIVES OF XYLOSE

BY CHARLES D. HURD AND LLOYD L. ISENHOUR

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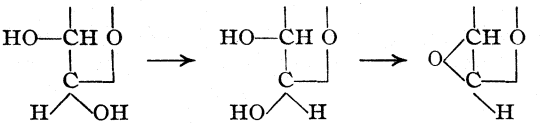
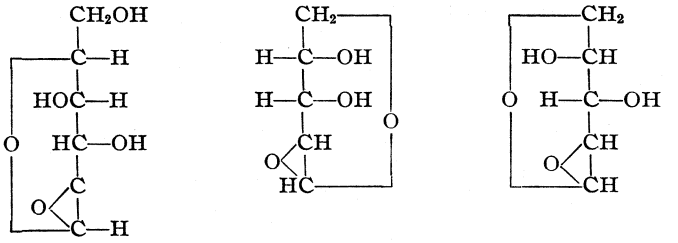
The transformation of xylose into furfural is a dehydration of an entirely different type from the one which xylose undergoes when it is heated alone. Only about 1% of furfural is formed in the latter case and the major product is xylosan: $C_5H_{10}O_5 \longrightarrow C_5H_8O_4 + H_2O$. This synthesis of xylosan from *α-d*-xylose is comparable to the production of glucosan from *α-d*-glucose[1] or arabinosan from *β-l*-arabinose.[2] All three of these sugars have adjacent hydroxyls on carbon atoms 1 and 2. Evidently this is essential, for *α-l*-arabinose, which does not, rearranges into the *β*-isomer before dehydration occurs



The ethylene oxide structure has been assumed in the case of glucosan and arabinosan. The same is assumed in the present paper for xylosan.



Glucosan Arabinosan Xylosan

From these structures, it would appear that the properties of xylosan and glucosan should be comparable. Xylosan showed the normal molecular weight in cold glacial acetic acid, but in water it was trimolecular. Warming the acetic acid solution to the boiling point of water caused polymerization, which changed the colorless solution to brown. Accordingly the best way to isolate the xylosan is to precipitate it from cold glacial acetic acid solution with ether. Attempts were made to crystallize it from acetic acid by evaporating at a low temperature, but the polymer was obtained in every case. The latter is a brown, wax-like substance. Xylosan yielded furfural when it was distilled with 12% hydrochloric acid, but only three-fourths of the theoretical amount was formed in twenty-four hours. Xy-

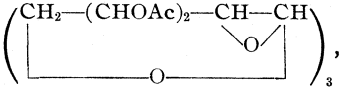
[1] Pictet and Castan, *Helv. Chim. Acta*, **3**, 645 (1920); Cramer and Cox, *ibid.*, **5**, 884 (1922); Pictet and Vogel, *ibid.*, **9**, 806 (1926).

[2] Vogel, *ibid.*, **11**, 1210 (1928).

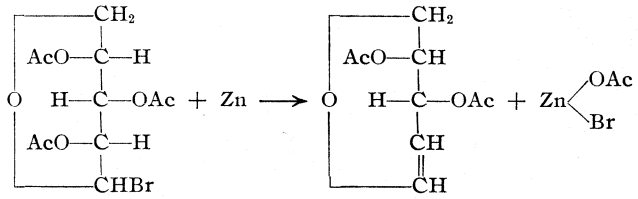
losan was easily oxidized. These properties of xylosan differ somewhat from the properties of glucosan as recorded by Pictet and Castan. They reported glucosan to be crystalline, deliquescent and soluble in water, evidently to a colorless solution. Since $\alpha$-glucosan is so much more stable than 3,4,6-triacetylglucose anhydride, of which it would be the parent, Hickinbottom[3] has questioned the C—C ring in the former. Furthermore,



Brigl and Schinle[4] were unable to synthesize glucosan in a crystalline state. Glucosan was prepared in this investigation and its properties were found to be very similar to those of xylosan. Both were deliquescent solids. Both dissolved in water giving a brown colored solution and both gave colorless solutions in acetic acid. Like xylosan, glucosan reduced Fehling's solution readily and dilute neutral potassium permanganate solution instantly.

**Diacetylxylosan.**—Acetylation of xylosan by a cold mixture of acetic anhydride and pyridine yielded diacetylxylosan. This compound is precipitated by dilution with water as an amorphous white solid. A brown solution is obtained in benzene or chloroform just as when xylosan is dissolved in water. Cryoscopic molecular weight determination in benzene showed that polymerization into a trimer,  , had occurred.

**Diacetylxylal.**—Bromoacetylxylose was synthesized from xylose and acetyl bromide and on reduction with zinc dust yielded diacetylxylal, a synthesis which has recently been described by Levene and Mori.[5]



Benzoyl hydrogen peroxide is known to convert a carbon-to-carbon double bond into an ethylene oxide derivative. The same reaction takes place with unsaturated carbohydrate derivatives as, for example, with such compounds[6] as glucal, rhamnal and cellobial. With diacetylxylal, oxidation of this type should yield diacetylxylosan or diacetyllyxosan, or a mixture of both. Actually, perbenzoic acid reacted with diacetylxylal to give

[3] Hickinbottom, *J. Chem. Soc.*, 3143 (1928).

[4] Brigl and Schinle, *Ber.*, **62,** 1716 (1929).

[5] Levene and Mori, *J. Biol. Chem.*, **83,** 803 (1929).

[6] Bergmann and Schotte, *Ber.*, **54,** 440, 1564 (1921); Tanaka, *Bull. Chem. Soc. Japan*, **5,** 214 (1930).

a white solid possessing many of the characteristics of the diacetylxylosan. Thus the material dissolved in acetic acid to form a colorless solution, while in chloroform or benzene it dissolved with production of a brown coloration. This color interfered with polarimetric readings, but it is certain that the observed rotation was lower than that of diacetylxylosan. Both substances on heating in a capillary tube polymerize to give a brown substance. There is a shrinkage in volume but no apparent melting. Differing from this, a mixture of the two melts as it polymerizes. Thus, it seems evident that other products than diacetylxylosan are also present. These could include diacetyllyxosan or even 1-benzoyl-3,4-diacetylxylose. Due to the small quantity available, this point could not be established with certainty. The material on hydrolysis gives a product which, with phenylhydrazine, yields phenylxylosazone, a change typical of either xylose or lyxose.

## Experimental Part

**Xylosan.**—Twelve grams of xylose was heated in a boiling xylene vapor-bath under 2 mm. pressure. Water was immediately liberated as shown by the heat generated in a phosphorus pentoxide trap. After one hour the mass started to melt and at the end of one and one-half hours the whole was bubbling vigorously. This continued for about twenty hours, after which period the xylose had acquired a dark caramel color. A loss in weight of 1.4 g. or 12% of the weight of the sugar occurred, corresponding to slightly more than one equivalent of water. Traces of furfural were detectable in the distillate by colorimetric methods.

The residue in the reaction tube was dissolved by boiling with several portions of glacial acetic acid. Although only a small amount of hot acetic acid was required to effect complete solution of xylosan, a gummy precipitate resulted if such a solution was cooled. To prevent this, the hot solution was poured into enough additional cold glacial acetic acid (500 cc.) to hold the xylosan in solution. An amorphous, cream-colored precipitate formed. On settling overnight, a gummy mass which was discarded formed in the bottom of the container. When the solution was decanted into two volumes of ether a flocculent, white precipitate separated which settled rapidly. The product was filtered in a dry atmosphere to prevent polymerization. This was accomplished by covering the Buchner funnel filtration system with a bell jar at the bottom of which calcium chloride was spread. The suspension to be filtered was added through the top of the jar by means of a separatory funnel.

The xylosan was washed on the filter with a little alcohol, then with an alcohol–ether mixture, and finally with 100 cc. of dry ether. It was dried in a vacuum desiccator over phosphoric anhydride. The yield of white, granular solid was 5.5 g., or 52% of the theoretical.

The product is very soluble in water, giving a brown colored solution. Xylosan is very soluble also in glacial acetic acid. This solution is colorless, but turns brown at 100°. It dissolves appreciably in ethylene glycol, hot ethyl alcohol, methyl alcohol, acetone and cold acetic acid and is insoluble in ether and chloroform. Xylosan reduces cold, neutral potassium permanganate solution instantly.

*Rotation.* Subs., 0.5138, in water to make 100 cc., 0.6804 g.; rotation +0.35, +0.47° (1-dm. tube, sodium light); $[\alpha]_D$ +68.1, +68.3°. After three weeks, the rotation of the second was +0.48, $[\alpha]_D$ +68.4°, showing an absence of mutarotation.

*Mol. wt.* in water: Subs., 0.1945 in 30 g. of water; f. p. lowering, 0.031°. Calcd.

for $(C_5H_8O_4)_3$: 396. Found: 398. *Mol. wt.* in acetic acid: Subs., 0.1059 in 30 g. of glacial acetic acid; f. p. lowering, 0.110°. Calcd. for $C_5H_8O_4$: 132. Found: 124.

*Anal.* (By F. D. Pilgrim) Subs., 0.1673, 0.1561: $CO_2$, 0.2764, 0.2512; $H_2O$, 0.1008, 0.0923. Calcd. for $C_5H_8O_4$: C, 45.2; H, 6.1. Found: C, 44.3, 44.0; H, 6.65, 6.59. Xylosan is very hygroscopic, making it difficult to obtain an accurate analysis.

**Furfural Formation.**—A solution of 0.1945 g. of xylosan was steam distilled for twenty-four hours with 12% hydrochloric acid. At the end of that time furfural was coming over in very small amounts. A colorimetric analysis[7] of the distillate showed 0.1067 g. of furfural formed. The theoretical yield was 0.1411 g. This slow formation of furfural indicates that the xylosan hydrolyzes very slowly.

**Melting Point Determination.**—At 95–97° and atmospheric pressure, the white, unimolecular form of xylosan changed to a dark brown solid with a definite shrinkage in volume, the latter at 205–210° being converted into another form without melting. A special melting point tube was then made by drawing one end of a 5-mm. tube to a capillary, which was sealed off. On heating the product under these conditions, at 0.3 mm. there was a slight darkening and shrinkage in volume at 119–20°, with apparent conversion into a new product at 163–165°. This last material was similar in appearance to that obtained at 95° under atmospheric pressure.

**Diacetylxylosan.**—Four grams of xylosan was dissolved in 20 cc. of cold pyridine and 20 g of cold acetic anhydride added and the mixture kept in a refrigerator for seventy-two hours at −3° and then poured into ice water. It was stirred with ice, filtered, dissolved in cold acetic acid and again filtered into ice water. It was then filtered by suction and washed with water, yielding a somewhat gummy solid which after standing for a few days in a vacuum desiccator over sulfuric acid became white and powdery. The solutions of diacetylxylosan in chloroform or benzene were brown in color and in acetic acid, colorless. This suggested, as with xylosan, that the brown solution contained a polymeric modification and that the colorless solution in acetic acid held unpolymerized diacetylxylosan.

*Rotation.* Subs., 1.000, in chloroform (U. S. P.) to make 10 cc.; rotation, +3.8° (1-dm. tube, sodium light); $[\alpha]_D$ +38.0°.

*Mol. wt.* Subs., 0.1603 in 10 g. of benzene; f. p. lowering, 0.126°. Calcd. for $(C_9H_{12}O_6)_3$: 648. Found: 651.

*Anal.* Subs., 0.3000: cc. of 0.1 *N* NaOH = acetic acid formed by hydrolysis, 27.8. Calcd. for $C_9H_{12}O_6$: acetyl, 39.81. Found: 39.85.

Diacetylxylosan darkened at 88–89 and at 95–100° became much darker and underwent a shrinkage in volume, polymerization apparently occurring at this point.

**Bromotriacetylxylose** was prepared from xylose essentially by Dale's[8] method. This was converted into diacetylxylal by reduction with zinc dust, using 50% acetic acid at −15° as the solvent. Since our preparation of diacetylxylal, Levene and Mori's[9] record of its synthesis has appeared.

*Anal.* Subs., 0.3520: cc. of 0.1 *N* NaOH, 35.1. Calcd. for $C_9H_{12}O_5$: acetyl, 43.0. Found: 42.9.

**Oxidation of Diacetylxylal with Perbenzoic Acid.**—Into a thoroughly dried suction flask was placed 1.5 g. of diacetylxylal. A chloroform solution of perbenzoic acid, prepared by the method of Hibbert and Burt[10] was filtered into the flask with suction.

[7] Youngburg and Pucher, *J. Biol. Chem.*, **61**, 741 (1924).

[8] Dale, THIS JOURNAL, **37**, 2745 (1915).

[9] Levene and Mori, *J. Biol. Chem.*, **83**, 803 (1929).

[10] Hibbert and Burt, THIS JOURNAL, **47**, 2240 (1925).

The suction was stopped before the last portion of the solution went through the filter to avoid drawing any moist air into the flask. The flask was tightly stoppered and shaken for a few minutes. When the diacetylxylal had completely dissolved, the mixture was left for twenty-four hours at 0°. It was then washed with ice water, followed by ice-cold sodium bicarbonate solution, and finally twice more with ice water. The chloroform solution was dried with calcium chloride, after which the solvent was removed *in vacuo*. The residue was taken up in 10 cc. of glacial acetic acid and the solution poured into 500 cc. of ice water. The white precipitate which formed was collected on a filter, washed with water, and dried in a vacuum desiccator over phosphoric anhydride. This product weighed 0.3382 g. An attempted melting point determination showed that it polymerized at 93–94°, uncorr.

The optical rotation in chloroform could not be measured because the solution was too brown to permit of observation. With a one decimeter tube the possible rotation was less than the error of observation.

*Anal.* Subs., 0.2755: cc. of 0.1 *N* alkali equivalent to the acetic acid formed, 12.5. Calcd. for $C_9H_{12}O_6$ (diacetylxylosan or diacetyllyxosan): acetyl, 20.0; calcd. for diacetylxylose: acetyl, 18.5. Found: 19.5.

**Xylosazone Formation.**—The residual solution from the acetyl determination was made neutral to litmus with sodium carbonate, and was then evaporated *in vacuo* to 10 cc. Two grams of sodium acetate and 1 g. of phenylhydrazine hydrochloride were added. The solution was allowed to stand for forty-five minutes at room temperature and was then heated in a boiling water-bath for two hours. After being left to cool overnight, 0.095 g. of yellow crystals formed which were carefully collected, washed with water and dried. The melting point of 153.4° (uncorr.) identified the substance as xylosazone. A mixed melting point with xylosazone also gave a value of 153°.

**Glucosan.**—Glucose (28.50 g.) was pyrolyzed in a 100-cc. round-bottomed flask according to the directions of Pictet and Castan.[1] The flask was evacuated to 13–15 mm. pressure and was then placed in an oil-bath which was adjusted to a temperature of 152–155°. The glucose melted and then began to bubble vigorously, giving off vapor. After three hours all reaction had ceased. The loss in weight, corresponding to one molecule of glucose minus one molecule of water, was 4.52 g. The residue was a slightly brown, wax-like substance. Attempts to crystallize it from absolute methanol were unsuccessful, but no extended efforts in this direction were carried out. The glucosan was very soluble in water and acetic acid, giving a brown colored solution in the former. It was slightly soluble in alcohol, giving a brown solution. It reduced Fehling's soluton readily and dilute, neutral potassium permanganate solution instantly. Its water solution decolorized bromine water instantly. Pouring a cold acetic acid solution into ether gave a flocculent, white precipitate. Cooling a hot, saturated solution in acetic acid caused a brown, gummy mass to separate. When left in the open air the product rapidly absorbed moisture. In all these characteristics, the glucosan was identical with the similarly prepared xylosan.

## Summary

Xylosan is formed by the pyrolysis of xylose. It is easily oxidizable. It polymerizes to a brown-colored trimer in aqueous solution, but in acetic acid solution it remains in the unpolymerized, colorless state. Diacetylxylosan shows the same tendency to polymerize in solvents other than acetic acid. Diacetyllyxosan, or a mixture of it with diacetylxylosan, is formed by the action of benzoyl hydrogen peroxide on diacetylxylal.

Glucosan, prepared in the manner of xylosan, has properties which closely resemble xylosan.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# THE MECHANISM OF CARBOHYDRATE OXIDATION. XV.[1] THE BEHAVIOR OF 3-GLUCOSIDO-ARABINOSE HEPTA-ACETATE TOWARD AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE

BY WM. LLOYD EVANS AND CHARLES C. CLARK

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It has been shown recently that there is a marked difference in the behavior of the 4-hexosido-glucoses and the 6-hexosido-glucoses toward aqueous solutions of potassium hydroxide.[1] These differences were attributed principally to the following general causes: (a) the chemical character of the hexosido section of the disaccharide molecule; and (b) the point of the hexosidic attachment. When maltose and cellobiose are acted upon by aqueous solutions of potassium hydroxide, it is found that the yields of lactic acid from these two disaccharides are about one-half as much as one would expect from an equivalent solution of glucose. In seeking an explanation for this latter fact through the application of the enediol theory of chemical behavior in the carbohydrates, it was shown that maltose and cellobiose should form a 3-glucosido-arabinose and formaldehyde as their first decomposition products in each case. Therefore, it becomes evident that these intermediate 3-glucosido-arabinoses obtained from maltose and cellobiose should be expected to show the same general reaction toward aqueous solutions of potassium hydroxide as did the original disaccharides under the same experimental conditions. If this assumption is correct, then in the alkaline decomposition of the 3-glucosido-arabinoses one should obtain pyruvic aldehyde, lactic and formic acids in yields of approximately the same order of magnitude as those obtained from cellobiose and maltose. To establish these points experimentally was the principal objective in this work.

## Experimental Part

**Cellobiose Octa-acetate.**—The method used for the preparation of cellobiose octa-acetate was essentially that described by Zemplén.[2] If the heat of reaction was insufficient to cause the temperature to rise to 100°, the mixture was heated on an electric hot-plate to that point. Our experience coincided with that of Haworth and Hirst,[3,4] who found that it was better to judge the progress of the reaction by the color of the

[1] Contribution XIV of this series, THIS JOURNAL, **53**, 4384 (1931).

[2] Zemplén, *Ber.*, **59**, 1254 (1926).

[3] Haworth and Hirst, *J. Chem. Soc.*, 2809 (1927).

[4] *Cf.* Haworth, Hirst, Streight, Thomas and Well, *ibid.*, 2636 (1930).

reaction mixture rather than by its temperature alone; *i. e.*, when the color is changing rapidly from a light to a dark red the reaction should be stopped. The yellowish-brown gummy precipitate that separated upon pouring the reaction mixture into water was allowed to stand overnight, after which it was filtered by suction, washed twice with water and then recrystallized once from twice its weight of alcohol–acetic acid mixture (5:1), according to the method of Levene and Wolfrom.[5] The average yield was 12 g. (m. p. 221°) from 60 g. of filter paper.

**Cellobiose.**—Cellobiose was prepared from the octa-acetate by the method of Zemplén.[2] The yields obtained in this procedure varied from 80–90%.

**Preparation of 3-Glucosido-arabinose Hepta-acetate.**—The procedure used was that of Zemplén.[2] A modification introduced by Levene and Wolfrom[5] in the preparation of cellobiose oxime was employed, *viz.*, calcium carbonate was used in evaporating the reaction mixture *in vacuo* to avoid the presence of free acid. The oxime was crystallized by nucleation.

**Treatment of 3-Glucosido-arabinose Hepta-acetate with Potassium Hydroxide.**—Eight-tenths gram (0.25 *M*) samples of crystalline 3-glucosido-arabinose hepta-acetate (m. p. 193°) were agitated with 5.27 cc. of potassium hydroxide solutions of the appropriate normalities at 25 and 50° for forty-eight hours. The procedure adopted was the same as that previously employed in this Laboratory for work of the same type,[6] with the exception that this is the first time that the acetate of a sugar has been employed in an investigation of this nature. Its use was necessitated because the non-acetylated carbohydrate could not be crystallized. Consequently, the alkaline solutions had to be of sufficient normality to deacetylate the acetate and also to react with the free sugar. In the experiments with mixtures of sugar acetates, 0.515 g. of glucose penta-acetate and 0.42 g. of arabinose tetra-acetate were used.

**Formic and Acetic Acids.**—Formic acid was determined by the method previously described.[6] The amount of acetic acid formed from the enolic splitting of 3-glucosido-arabinose was too small to be determined accurately by difference in the presence of the large amount of this same acid produced by the saponification of the acetate. For this reason no attempt was made to secure data for acetic acid.

**Pyruvic Aldehyde Osazone.**—The osazone experiments were carried out in the same manner as described in previous papers[6] except that 0.8-g. samples of the sugar derivative were employed because of the scarcity of the material. The volume of standard potassium hydroxide solution was 5.27 cc., that of phenylhydrazine 1.09 cc., and alcohol (95%) 3.70 cc. In determining the normality of the potassium hydroxide solutions, corrections were applied for the volume of the alcohol and the phenylhydrazine.

**Lactic Acid.**—This acid was determined by a method developed by G. F. Nadeau[7] of this Laboratory. The details which are to be published later are essentially as follows. Barium carbonate is used instead of zinc carbonate as the compound over which the ether extract of lactic acid is collected. The residue remaining after the evaporation of the ether was treated with water and the insoluble barium carbonate removed. The filtrate containing the soluble barium lactate was evaporated to dryness on a steam-bath. The barium lactate was removed from the salt mixture by means of 80% alcohol and the resulting solution was analyzed for its barium content.

**Experimental Data.**—Our experimental data are given in graphical form in Figs. 1–5.

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[5] Levene and Wolfrom, *J. Biol. Chem.*, **77**, 677 (1928).

[6] Evans and Benoy, THIS JOURNAL, **52**, 294 (1930).

[7] G. F. Nadeau, Dissertation for the Ph.D. degree, The Ohio State University, March, 1931.

## Discussion and Summary

**Theory.**—It has been pointed out by Benoy[6] and Hockett[1] and one of us that the 3-glucosido-arabinoses obtained in the decomposition of the 1,2-enediols of maltose and cellobiose should undergo in turn the same kind of changes in aqueous solutions of potassium hydroxide as the disaccharides themselves do. In these substituted pentoses, as in maltose and cellobiose, there is still present the hindering action[8,1] which arises from the point of glucosidic attachment (carbon atom 3), which necessarily imposes a limit on the number of enediols which may possibly form under these circumstances. It is conceivable that these 3-glucosido-arabinoses may undergo decomposition reactions in three possible ways: (a) the pentose derivative may hydrolyze, thus giving rise to glucose and arabinose; or (b) there is no *a priori* reason why the 3-glucosido-arabinoses should not be converted to the corresponding 3-glucosido-arabinuloses and 3-glucosido-riboses through the well-known de Bruyn and van Ekenstein rearrangement,[9] a reaction which would be followed by the formation of a common 3-glucosido-pentose-1,2-enediol; and (c) both reactions (a and b) may take place simultaneously. A comparison of the relative amounts of pyruvic aldehyde, lactic and formic acids obtained from alkaline solution of 3-glucosido-arabinose hepta-acetate from cellobiose with the quantities of the same products obtained from maltose, cellobiose, glucose and a mixture of glucose penta-acetate and arabinose tetra-acetate, is best understood on the general basis outlined in this paragraph, and also from the following more detailed statement of the mechanism.

**Lactic Acid.**—If 3-glucosido-arabinose hepta-acetate (from cellobiose) undergoes a rapid hydrolysis in aqueous solutions of potassium hydroxide such as one would expect in acid solutions, then both the hexose and pentose sugars thus formed would become sources[10] for the production of lactic acid. Under these circumstances the amount of this acid should more nearly approximate that obtained from an equivalent mixture of glucose pentaacetate and arabinose tetracetate[11] as shown in Fig. 1. However, a comparison of the data obtained from the reaction mixture of these two acetates with those obtained from the 3-glucosido-arabinose hepta-acetate shows that the latter sugar derivative yields but approximately half of the lactic acid one should expect if the 3-glucosido-arabinose hepta-acetate had first undergone complete hydrolysis. Obviously, one must conclude,

[8] Lewis and Buckborough, THIS JOURNAL, **36**, 2385 (1914); Nef, *Ann.*, **403**, 204 (1914).

[9] De Bruyn and van Ekenstein, *Rec. trav. chim.*, **14**, 156, 203 (1895); **15**, 92 (1896); **16**, 257, 262, 274 (1897); **19**, 1 (1900); **27**, 1 (1908). *Cf.* Gross with Lewis, THIS JOURNAL, **53**, 2772 (1931).

[10] Evans and O'Donnell, *ibid.*, **50**, 2543 (1928); Evans and Conaway, *ibid.*, **52**, 3680 (1930).

[11] Hudson and Dale, *ibid.*, **40**, 994 (1918).

therefore, that the reaction mechanism for the production of lactic acid through the preliminary hydrolysis of 3-glucosido-arabinose is not wholly adequate and, indeed, accounts for but a small fraction of this product. The other alternative lies in the further decomposition of 3-glucosido-arabinose into 2-glucosido-erythrose and hydroxymethylene and the

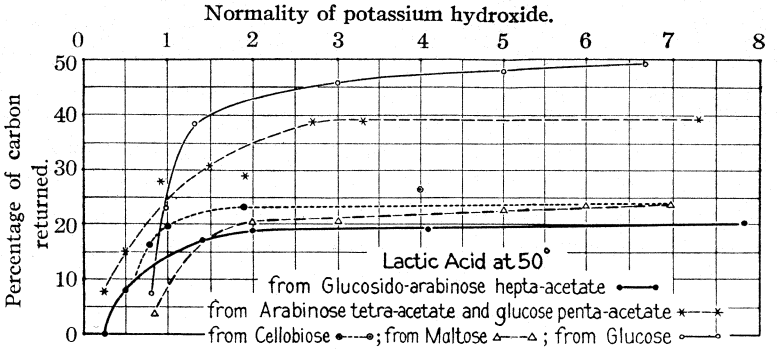
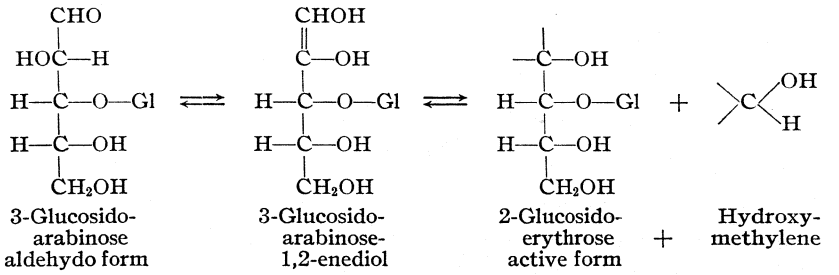



Fig. 1.

subsequent hydrolysis of the tetrose derivative as shown by the following reactions in which it is assumed that a complete deacetylation had taken place previously.




These reactions show that it is theoretically possible for glucose to be formed as a reaction product through a series of steps that would be equivalent to changing the pentose section of the reacting molecule into one of a tetrose sugar and one of hydroxymethylene. This, in effect, would remove the possibility of the arabinose being a source of lactic acid because

it has been shown by Hutchman[12] of this Laboratory, that no lactic acid is formed in alkaline solutions of glycol aldehyde, solutions which Fischer and Landsteiner[13] have shown certain tetrose sugars. From these facts it follows that the lactic acid produced in the action of aqueous solutions of potassium hydroxide on 3-glucosido-arabinose hepta-acetate must be derived from the hexosido section of the molecule. This conclusion is in complete harmony with the following experimental facts. (a) Lactic acid is formed in aqueous solutions of the hexoses in the presence of potassium hydroxide and in amounts that are dependent upon the original alkali normality of the solutions and the temperature employed, factors[10] which also seem to play an important role in the alkaline decomposition of 3-glucosido-arabinose. (b) Lactic acid is also found in the alkaline solutions of cellobiose and maltose (Fig. 1) in amounts that harmonize with the postulate that the hexosido section of these molecules is the source of this

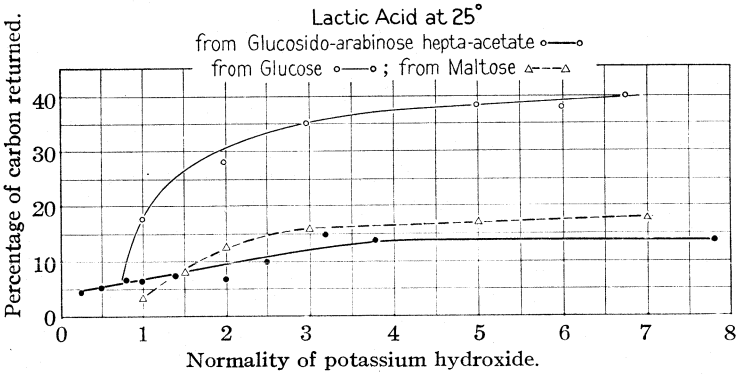



Fig. 2.

product, *i. e.*, the amounts of lactic acid obtained from these two disaccharides were found to be approximately one-half those derived from an equivalent solution of glucose under the same experimental conditions. The yields of lactic acid in these latter cases are also dependent upon the experimental factors given in (a). The effect of temperature on the production of lactic acid from alkaline solutions of maltose, glucose and 3-glucosido-arabinose hepta-acetate may be seen by comparing the data given in Figs. 1 and 2.

From these considerations it is seen that the behavior of 3-glucosido-arabinose toward aqueous solutions of potassium hydroxide harmonizes with the postulate that this pentose derivative is an intermediate compound in the alkaline degradation of cellobiose and maltose; *i. e.*, as is shown by

[12] J. E. Hutchman, Dissertation for the Ph.D. degree, The Ohio State University, 1927; *cf.* Ref. 1.

[13] Fischer and Landsteiner, *Ber.*, **25**, 2549 (1892).

our experimental data in Fig. 1, the amount of lactic acid obtained from the alkaline degradation of 3-glucosido-arabinose hepta-acetate is approximately the same as that derived from these two disaccharides under the same experimental conditions.

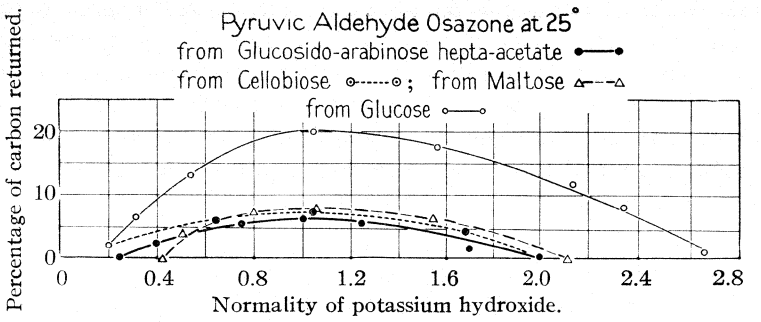



Fig. 3.

**Pyruvic Aldehyde.**—Since pyruvic aldehyde is regarded as the forerunner of lactic acid formation in the action of alkalies on the carbohydrates, it was to have been expected that the amounts of pyruvic aldehyde osazone formed from 3-glucosido-arabinose hepta-acetate should

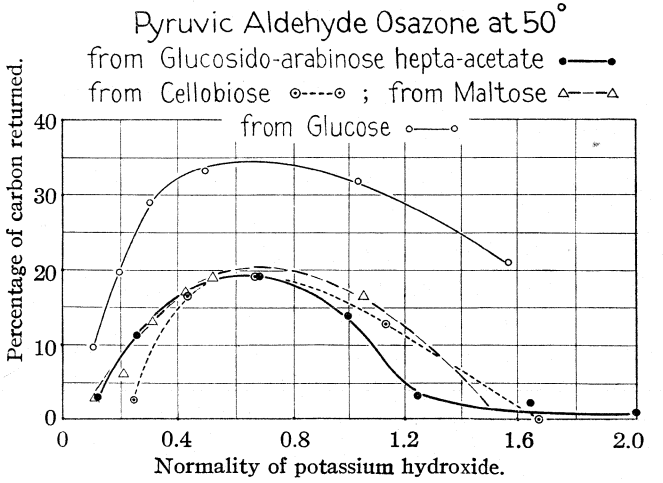



Fig. 4.

show the same general relationship to the yields of this derivative obtained from glucose, cellobiose and maltose as in the case with the yields of lactic acid. That this seems to be true at 25 and 50° is shown in Figs. 3 and 4, respectively.

**Formic Acid.**—The sources of formic acid in the alkaline degradation of the disaccharide sugars have been pointed out previously.[1,6,10] It was

shown that the yields of formic acid from the 4-hexosido-glucoses are higher than those obtained from the 6-hexosido-glucoses. Since the formation of 3-glucosido-arabinose from cellobiose and maltose is accompanied by hydroxymethylene formation, the relative amount of formic acid obtained from the pentose derivative should, in general, be less than that from the disaccharides. In Fig. 5 a comparison is shown of the yields of formic acid obtained from maltose, cellobiose and 3-glucosido-arabinose. At approximately 3.2 *N* and 2 *N* potassium hydroxide it is seen that the yields of formic acid from maltose and cellobiose, respectively, tend toward lower values than those obtained from the glucosido hepta-acetate. This unexpected

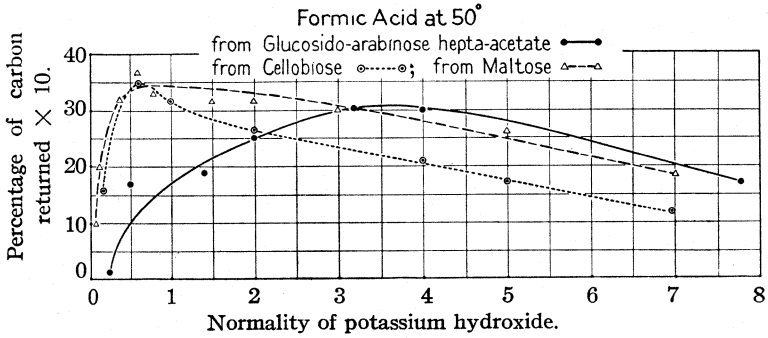



Fig. 5.

behavior in the region of higher alkalinities may be due to an equilibrium condition whereby the two well-known disaccharides now begin to form appreciable amounts of their 2,3-enediol which on rupture at the double bond would yield glycol aldehyde and 2-glucosido-erythrose. This shifting in the alkaline system would tend to lower the concentration of hydroxymethylene molecules, and hence the formic acid yields. By reason of the hindering action of the hexosido section of the molecule, the glucosido-arabinose cannot form a 2,3-enediol and hence its alkaline decomposition up to the point of hydrolysis must yield hydroxymethylene continuously. The fact that alkaline solutions of glycol aldehyde of sufficient molar strength will also yield formic acid must not be overlooked in seeking a sound explanation for the above behavior of glucosido-arabinose hepta-acetate.

Owing to the extreme complexity of the reaction mixtures in each of these cases it has been found difficult to determine quantitatively the small amounts of formic acid in the presence of so much acetic acid, with an accuracy such as we would desire. Hence, these data with reference to formic acid are valuable as indicating the tendency of the reaction.

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[CONTRIBUTION NO. 222 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

# SYNTHETIC GLYCERIDES. III. MIXED TRIGLYCERIDES OF THE DISTEARIN SERIES

BY H. E. ROBINSON, J. N. ROCHE AND C. G. KING

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In previous communications[1] on synthetic glycerides it was pointed out that much of the information reported in the literature was faulty and that reliable constants were not available for the identification of natural fatty acid glycerides. Experimental work indicated that the melting points and refractive indices of symmetrical isomers were definitely higher than those of the unsymmetrical forms. In continuing the study, six sets of isomeric mixed triglycerides of the distearin series have been prepared and their melting points and refractive indices determined. Quantitative solubility determinations have also been made on representative pairs.

Progress in the study of the components of naturally occurring fats is in part dependent upon the synthesis of fatty acid glycerides of known constitution and the determination of their chemical and physical properties.

A critical study of methods used for the preparation of glycerides and the correlation of available data on their physical properties should bring out definite relationships between the constitution of the fats and their physical properties. In the past the methods of synthesis of the glycerides have varied greatly and the products of the reactions have not always been definitely characterized. In many cases where pure compounds were thought to have been formed, it is probable that mixtures or unexpected isomers were formed.

A review of the literature readily shows the need for the preparation and determination of physical constants of glycerides of proved configuration. Fischer's work[2] on the shifting of acyl groups in glycerides did much to stimulate interest in clarifying and extending the data on the preparation and properties of such compounds.

The greatest discrepancies in the synthesis of glycerides have appeared in the cases where so-called $\beta$-monoglycerides and $\alpha,\beta$-diglycerides were utilized as intermediate compounds. Fairbourne and Foster[3] have shown experimentally that $\beta$-monoglycerides prepared from $\beta$-monochlorohydrin and the potassium salts of fatty acids by the method reported by Grün,[4] or some modification thereof, are identical with the $\alpha$-compounds. The

[1] J. N. Roche, H. P. Averill and C. G. King, THIS JOURNAL, **51**, 866 (1929); **52**, 365 (1930).

[2] E. Fischer, *Ber.*, **53**, 1621 (1920).

[3] A. Fairbourne and G. E. Foster, *J. Chem. Soc.*, 3148 (1926).

[4] Grün, *Ber.*, **43**, 1288 (1910).

trigylcerides prepared from such β-monoglycerides are therefore probably the unsymmetrical isomers.

Delaby and Dubois,[5] from a study of the reactions between glycerol and formic acid, reported the synthesis of α,β- and α,α′-diformates of glycerol. The probable identity of these compounds is indicated by the investigations of Fairbourne[6] on α,β- and α,α′-diglycerides. From the results of Fairbourne's investigations, it would seem very doubtful that an unsymmetrical diglyceride has ever been isolated in pure form. Syntheses of unsymmetrical triglycerides based on the use of α,β-diglycerides would seem questionable in like degree.

Helferich and Sieber[7] have apparently made a true β-monobenzoate by a method which will probable be applicable to other β-type esters. Hill, Whelen and Hibbert[8] have synthesized the true β-methyl ether, probably the first β-ether of proven constitution ever isolated. It is noteworthy that the compound is reported to be comparatively stable.

From a consideration of the slight difference in the physical constants of the isomeric α- and β-monomargarins reported by Thomson[9] and the doubtful method of preparation of the symmetrical compound, it is probable that these compounds are identical. The same criticism may be made regarding the α,β- and α,α′-dimargarins reported by Thomson.

Fairbourne[6] has shown that all preparations of α,β-distearin from α,β-dichloro- and α,β-dibromohydrins are identical with α,α′-distearin prepared in an analogous manner from α,α′-dihalohydrins. Fischer's work[2] on the symmetrical structure of distearin prepared from α-iodo-α′,β-distearin offers an explanation for the probable symmetrical structure of nearly all so-called unsymmetrical diglycerides of fatty acids which have been reported in the literature. The experiments of Grün and Limpacher[10] on the optical activity of α,β- and α,α′-diglycerides do not appear to permit any definite conclusions, probably because adequate methods for the preparation of α,β-diglycerides were not available.

The use of α,β-acetoneglycerol which has been prepared by the condensation of acetone and glycerol in either neutral or acid medium, for the preparation of α-monoglycerides, is justified by the work of Irvine, MacDonald and Soutar[11] and Hibbert and Marazain.[12] The isomeric α,α′-acetoneglycerol has been prepared and its configuration proved by Carter.[13]

[5] R. Delaby and P. Dubois, *Compt. rend.*, **187,** 767 (1928).
[6] A. Fairbourne, *J. Chem. Soc.*, 369 (1930).
[7] B. Helferich and H. Sieber, *Z. physiol. Chem.*, **175,** 311 (1928).
[8] H. C. Hill, M. S. Whelen and H. Hibbert, THIS JOURNAL, **50,** 2235 (1928).
[9] W. F. Thomson, *Trans. Roy. Soc. Canada*, **20,** 445 (1926).
[10] Grün and R. Limpacher, *Ber.*, **59,** 1350 (1926); **60,** 147 (1927).
[11] J. C. Irvine, J. MacDonald and C. W. Soutar, *J. Chem. Soc.*, **107,** 337 (1915).
[12] H. Hibbert and J. G. Marazain, *Can. J. Res.*, **2,** 35 (1930).
[13] N. M. Carter, *Ber.*, **63B,** 2399 (1930).

A new method may be available for the synthesis of mixed triglycerides through the preparation and identification of β-monopalmitin by Bergmann and Carter.[14]

In the field dealing with the separation and identification of naturally occurring mixed triglycerides, the work of Hilditch and associates[15] is outstanding, particularly in view of the applicability of their procedures to the problem of establishing the configuration of mixed glycerides containing both saturated and unsaturated fatty acids. Proof of the structures of such derived products will also be in part dependent upon the availability of reliable methods of synthesis.

## Experimental

The absolute glycerol, acetone, chloroform, ethyl alcohol, ether, ethyl acetate and petroleum ether used in this work, were prepared by standard methods. The purity of all reagents used during the course of the investigation was carefully checked.

Acyl chlorides were prepared by the use of thionyl chloride and fatty acids as recommended by McMaster and Ahmann.[16] Caprylloyl chloride, b. p. 71–73° (6–7 mm.), capryl chloride, b. p. 105–107° (8–9 mm.), and stearyl chloride, b. p. 185° (3 mm.), were prepared by this method.

**Preparation of Intermediate Glycerides.**—α-Monocaproin was prepared by the method recommended by Schuette and Hale[17] for α-monobutyrin. Anhydrous glycerol (25 g.) was treated with 30 g. of caproic acid and 2 g. of phosphoric acid (85%). The final distillate showed a boiling point of 162° (4 mm.); yield 75%. α-Caproyl-acetone-glycerol, b. p. 124° (3 mm.), was prepared by the action of caproyl chloride on acetone-glycerol. On attempted hydrolysis with concentrated hydrochloric acid at −15° the compound decomposed.

An attempt to prepare α-monocaprylloin by the above method was unsuccessful. Direct esterification of glycerol with fatty acids of more than six carbon atoms as above described does not seem to be readily accomplished. The α-monocaprylloin used was prepared by Fischer's method. It distilled at 178–181° (5–6 mm.). α-Monocaprin, m. p. 51.2°, α-monolaurin, m. p. 63.2°, α-monomyristin, m. p. 67.5°, and α-monopalmitin, m. p. 77.0°, were prepared as described in a previous communication.

α,α -Distearin, m. p. 78.9°, was prepared from α-iodo-α′,β-distearin by hydrolysis with silver nitrite in boiling ethyl alcohol. In the purification of the α,α′-distearin, the addition of a small amount of sodium iodide solution was found to aid materially in the removal of traces of silver. This compound was also prepared by the action of sodium stearate on α,α′-dichlorohydrin. The melting points and mixed melting points of the two preparations were identical.

**Synthesis of Triglycerides.**—For the preparation of symmetrical mixed triglycerides the preparation of β-capro-α,α′-distearin is used as an example.

This compound was prepared by the slow addition of 0.68 g. of capryl chloride with 0.50 g. of quinoline to 2.0 g. of α,α′-distearin contained in a glass-stoppered iodine flask. The reaction mixture was dissolved in 10 cc. of chloroform and allowed to stand in an oven at 55° for forty hours. The chloroform solution was then taken up with 100 cc.

[14] M. Bergmann and N. M. Carter, *Z. physiol. Chem.*, **191**, 211 (1930).

[15] T. P. Hilditch and C. H. Lea, *J. Chem. Soc.*, 3106 (1927); G. Collin, T. P. Hilditch and C. H. Lea, *J. Soc. Chem. Ind.*, **48**, 46T (1929).

[16] L. McMaster and F. E. Ahmann, THIS JOURNAL, **50**, 147 (1928).

[17] H. A. Schuette and J. T. Hale, *ibid.*, **52**, 1978 (1930).

of ether and 60 cc. of half normal sulfuric acid and placed in a separatory funnel. The ether solution was washed successively with half normal sulfuric acid, 10% potassium bicarbonate solution and finally with distilled water. After several hours of drying over sodium sulfate, the triglyceride was precipitated from ether solution by cooling in an ice–salt bath at −20°. The white crystals were dried over phosphorus pentoxide *in vacuo*. After three recrystallizations from ether and from acetone the compound melted sharply at 56.2°; yield, 72%.

For the unsymmetrical mixed triglycerides, the α-monoglycerides were treated with two moles of stearyl chloride, using quinoline as a condensing agent. The unsymmetrical compounds were all prepared below 35°.

The melting points and refractive indices of the triglycerides prepared are listed in the following table.

TABLE I

MELTING POINTS AND REFRACTIVE INDICES

| Compound | M. p. found, °C. | $n_D^{70}$ | M. p. and R. I. previously recorded |
|---|---|---|---|
| α-Caproylo-α′,β-distearin | 42.7 | 1.43985 | New |
| β-Caproylo-α,α′-distearin | 47.2 | 1.44019 | New |
| α-Caprylo-α′,β-distearin | 47.6 | 1.44028 | New |
| β-Caprylo-α,α′-distearin | 51.8 | 1.44140 | New |
| α-Capro-α′,β-distearin | 48.2 | 1.44058 | New |
| β-Capro-α,α′-distearin | 56.2 | 1.44153 | New |
| α-Lauro-α′,β-distearin | 50.6 | 1.44098 | 47 and 49°,[a] 49–50°[b] |
| β-Lauro-α,α′-distearin | 59.8 | 1.44222 | 53.5 and 68.5°[c] |
| α-Myristo-α′,β-distearin | 58.5 | 1.44122 | 52 and 62[a] |
| β-Myristo-α,α′-distearin | 63.5 | 1.44300 | 55 and 57.5°[c] |
| α-Palmito-α′,β-distearin | 62.6 | 1.44245 | 63.2[d] |
| β-Palmito-α,α′-distearin | 68.0 | 1.44374 | 67.9°,[d] 64.8°,[e] $n_D^{70}$ −1.4467[e] |

Average $dn/dt$ for six unsymmetrical isomers, 0.00040
Average $dn/dt$ for six symmetrical isomers, 0.00041
Average difference in R. I. for six isomeric pairs, 0.00112
Average difference in m. p. for six isomeric pairs, 6.0°

[a] *Ber.*, **40**, 1795 (1907); [b] *ibid.*, **53**, 1589 (1920); [c] *ibid.*, **40**, 1781 (1907); [d] *Biochem. Z.*, **130**, 252 (1922); [e] *Proc. Roy. Soc. Canada*, **13**, 255 (1919).

Consideration of the data presented shows that in every case the symmetrical compounds have a higher index of refraction and a higher melting point than their unsymmetrical isomers. The melting points and refractive indices of the compounds are seen to be in order in the series. An immersion refractometer mounted in a constant temperature bath as described previously was used for all determinations. The values for the refractive indices given in the table were derived from graphs plotted from index readings over a range of about 10°. A consistent difference in refractive index was found for the two isomeric types, the symmetrical form being slightly higher, as found previously.

The molecular weights of all triglycerides prepared were found to check the theoretical values within the limits of experimental error. An accuracy of 1 to 2% was attained in the determination of molecular weights

using the ebullioscopic procedure with the differential thermometer perfected by Menzies and Wright.[18] Ethyl acetate was found to be the best solvent for the determinations.

**Determination of Quantitative Solubilities.**—It has been stated previously[1,2] as a qualitative observation that unsymmetrical triglycerides were somewhat more soluble than their symmetrical isomers, but no quantitative data have been recorded. It is evident that there is an appreciable difference in the solubility of the isomeric forms in the usual organic solvents. This difference in solubility should be of considerable assistance in the separation and identification of isomers.

Ten cc. of the solvent used was saturated at 50° with the glyceride and placed in a thermostat at the indicated temperature for several hours with constant shaking. One cc. of the saturated solution was withdrawn and evaporated to dryness in a weighing bottle.

TABLE II

SOLUBILITIES

| Compound | Solvent[a] | T, °C. | Solubility in grams per 100 cc. of solvent |
|---|---|---|---|
| α-Capro-α′,β-distearin | Acetone | 29.0 | 39.45 |
| β-Capro-α,α′-distearin | Acetone | 29.0 | 2.57 |
| α-Capro-α′,β-distearin | Alcohol | 27.5 | 0.22 |
| β-Capro-α,α′-distearin | Alcohol | 27.5 | 0.14 |
| α-Lauro-α′,β-distearin | Petr. ether | 27.5 | 38.41 |
| β-Lauro-α,α′-distearin | Petr. ether | 27.5 | 11.42 |
| α-Myristo-α′,β-distearin | Alcohol | 29.0 | 0.59 |
| β-Myristo-α,α′-distearin | Alcohol | 29.0 | 0.47 |
| α-Palmito-α′,β-dimyristin[b] | Alcohol | 27.5 | 0.42 |
| β-Palmito-α,α′-dimyristin[b] | Alcohol | 27.5 | 0.10 |
| α-Palmito-α′,β-dimyristin[b] | Acetone | 27.5 | 1.82 |
| β-Palmito-α,α′-dimyristin[b] | Acetone | 27.5 | 0.61 |

[a] All solvents used were anhydrous. [b] Prepared by Roche, Averill and King.[1]

## Summary

Isomeric triglycerides of the distearin series have been prepared containing the natural fatty acids from caproic to palmitic. Melting points, refractive indices, solubilities and molecular weights of the isomeric compounds have been determined.

It was found in every case that the melting point of the symmetrical compound is appreciably higher (average 6°) than that of the corresponding isomer. The melting points of the individual compounds are also in order in the series. The symmetrical isomers also have a measurably higher index of refraction (average 0.00112) and a lower solubility. The refractive indices of the isomers are also in order as a series.

The use of thionyl chloride for the preparation of acyl chlorides of

[18] A. W. C. Menzies and S. L. Wright, THIS JOURNAL, 43, 2312 (1921).

the fatty acids was found more satisfactory than the methods previously used. The removal of traces of silver from the diglycerides synthesized by Fischer's method has been simplified by the use of sodium iodide solution.

The synthesis and identification of the following compounds herein described have not been reported previously: α-monocaproin, α-monocaproyl-acetoneglycerol, and the isomeric caproyl-distearins, capryllo-distearins and capro-distearins.

PITTSBURGH, PENNSYLVANIA

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[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN DIVISION OF THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

# THE DEHYDROGENATION OF CERTAIN AMINES AND HYDRAZINES BY UNSATURATED COMPOUNDS (PRELIMINARY PAPER)

BY L. A. PINCK AND GUIDO E. HILBERT

RECEIVED SEPTEMBER 2, 1931 PUBLISHED FEBRUARY 5, 1932

The two theories of biological oxidation that probably have received most attention in recent years are those of Warburg[1] and of Wieland.[2] Warburg's theory is expressed as being a process in which the oxidation is catalyzed by iron. The active agent, "the respiration enzyme," is an iron complex of a compound related to hematin. Wieland's theory, which is definitely contradictory to that of Warburg, is pictured as being a transfer of hydrogen atoms from one molecule to the other. The oxidation is thus essentially a dehydrogenation. Wieland and Bergel[3] studied the oxidation of amino acids with animal charcoal and adduced evidence that the degradation takes place in the following manner

$$\mathrm{R{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}COOH} \xrightarrow{-2H} \mathrm{R{-}\underset{\displaystyle NH}{\underset{\|}{C}}{-}COOH} \xrightarrow{H_2O} \mathrm{R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}COOH} + NH_3$$

in which the first step consists of a removal of hydrogen atoms. The oxidation of amines, which has been the subject of considerable work, has usually been carried out by such drastic reagents as the hypohalites[4] and potassium permanganate,[5] oxidizers which presumably do not exist in biological systems. Additional evidence has now been obtained in favor of Wieland's mechanism of biological oxidation. The dehydrogenation has

[1] Otto Warburg, "Über die katalytischen Wirkung der lebendigen Substanz," Berlin, 1928.

[2] Wieland, *Ergebnisse Physiol.*, **20**, 477 (1922).

[3] Wieland and Bergel, *Ann.*, **439**, 196 (1924).

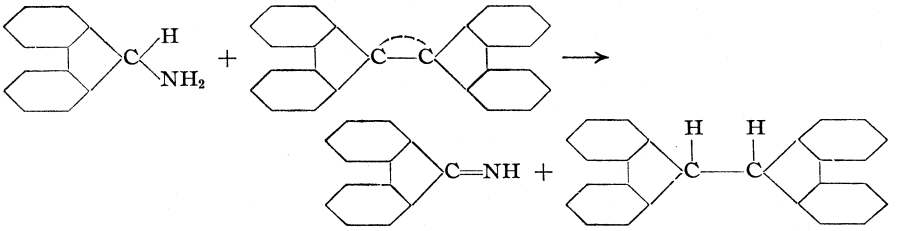
[4] Hofmann, *Ber.*, **14**, 2725 (1881); Stieglitz, and co-workers, THIS JOURNAL, **36**, 272 (1914); **38**, 2046 (1916); Hellerman and Sanders, *ibid.*, **49**, 1742 (1927).

[5] Goldschmidt and Beuschel, *Ann.*, **447**, 197 (1926); Goldschmidt and Reichel, *ibid.*, **456**, 152 (1927).

been accomplished under mild conditions by the use of various unsaturated substances, containing active groups, which are known to occur in nature. The imide, which according to Wieland's theory is the initial product formed, has been isolated as such.

Such compounds as dibiphenyleneethylene, azobenzene, indigo and methylene blue, in which the linkages C=C, N=N, C=O and C=N, respectively, are known to be highly active, can dehydrogenate 9-fluorylamine. Dibiphenyleneethylene is also effective in dehydrogenating hydrazobenzene.

The reaction between 9-fluorylamine and dibiphenyleneethylene was found to take place very smoothly in liquid ammonia and is expressed by the equation




The reaction goes to completion at room temperature and is readily followed visually by the gradual disappearance of the red ethylene compound. Liquid ammonia appears to be the ideal solvent for carrying out these reactions since possible complications by interaction between fluorenone imide and 9-fluorylamine to form the Schiff base are eliminated. Attempts to carry out the reaction in other solvents such as alcohol benzene and pyridine have thus far been unsuccessful.

It is interesting to note the marked change in the reactivity of dibiphenyleneethylene when either one or both of the biphenylene groups are replaced by other substituents. Thus, when one of the biphenylene groups was replaced by hydrogen and a phenyl group, as in the case of benzalfluorene, the reaction was incomplete even on heating for eight days at 60°, as compared with a complete reaction of dibiphenyleneethylene within two days at 40°. Upon the introduction of two phenyl radicals in place of a biphenylene group, the compound did not react at all. The same was found to be true of tetraphenylethylene. This is not surprising since it is well known that the double bond of tetraphenylethylene is relatively inert and does not show any tendency to add either bromine[6] or nitrogen dioxide.[7] Thiele and co-workers,[8] in a study of the reduction of un-

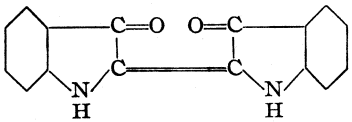
[6] Biltz, *Ann.*, **296**, 231 (1897); Bauer, *Ber.*, **37**, 3321 (1904).

[7] Schlenk, *Ann.*, **394**, 213 (1912). The nitrogen dioxide enters the benzene rings instead of adding on the double bond.

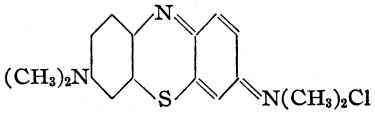
[8] Thiele, *Ber.*, **33**, 3395 (1900); Thiele and Bühner, *Ann.*, **347**, 249 (1906); Thiele and Rüdiger, *ibid.*, **347**, 275 (1906); Thiele and Henle, *ibid.*, **347**, 290 (1906).

saturated hydrocarbons with aluminum amalgam, found that such compounds as tetraphenylethylene, dimethylfulvene, 1,4-diphenylbutadiene and both dihydrocinnamylidenefluorenes were not reduced. Since aluminum amalgam is without doubt a stronger reducing agent than 9-fluorylamine, this group of compounds will also probably not be affected by the latter. On the other hand, not only dibiphenyleneethylene and benzalfluorene but also benzalindene, cinnamylidenefluorene, etc., some of which probably will also dehydrogenate the amine, are reduced by aluminum amalgam.

A number of the dyes and azo compounds are also excellent dehydrogenators. Of this group three were studied, indigo (I), methylene blue (II) and azobenzene. The reactivity toward 9-fluorylamine was found



I



II

to increase in the order dibiphenyleneethylene, indigo, methylene blue and azobenzene. In the case of the dyes, the end-products are the leuco bases, whereas azobenzene is reduced to hydrazobenzene, which was found to be stable toward the amine. It is of interest to note that all the dehydrogenators used in this work absorb light in the visible region of the spectrum. As the color of a substance indicates low energy electronic transitions, it is possible that this may have some relation to chemical reactivity.

Other compounds can also take the place of 9-fluorylamine in the above reactions and act as the source of hydrogen. Hydrazobenzene readily reacts with dibiphenyleneethylene; the end-products are dibiphenyleneethane and azobenzene. On allowing a solution of the amino acid tyrosine in liquid ammonia to interact with dibiphenyleneethylene, a slow reaction takes place, the results of which, however, will be published at a later date. On the other hand, benzhydrylamine, which is very similar in structure to 9-fluorylamine, is unaffected by any of the dehydrogenators. It appears that the ease of oxidation of 9-fluorylamine is a property conferred upon it by the five-membered ring, and depends upon its environment.

The fact that an active carbon–carbon double bond such as occurs in dibiphenyleneethylene can act as a dehydrogenator toward 9-fluorylamine and hydrazobenzene is new. There is no reason for believing that the reaction is necessarily limited to either an environment of liquid ammonia or to the fluorene type of compounds. It is probable that other very active carbon–carbon double bonds and free radicals will behave similarly, and that they will also be able to dehydrogenate compounds other than certain

amines and hydrazines. Since 9-fluorylamine and benzhydrylamine are easily oxidized by oxygen, it is peculiar but also significant that they should show such a difference in behavior toward the above dehydrogenators in liquid ammonia. It is hoped that further work will provide an explanation for this difference in behavior and also of the mechanism of the dehydrogenation.

## Experimental

**9-Fluorylamine.**—Wieland and Roseeu[9] in a cursory statement mentioned that the reduction of fluorenone ketazine on treatment with zinc dust in acetic acid yielded 9-fluorylamine. Kuhn and Jacob[10] later described the method in greater detail. As the procedure used by us differed somewhat from that of the previous investigators, its description is given here. It has been our experience that this is the best method for the preparation of 9-fluorylamine.

Fluorenone ketazine was prepared in the manner described by Wieland and Roseeu. A yield of 93.5 g. was obtained from 100 g. of fluorenone. A solution of 50 g. of fluorenone ketazine in 250 cc. of glacial acetic acid was treated with 80 g. of zinc dust and boiled for six hours. After filtration of the hot solution, the zinc residue was digested with boiling acetic acid and filtered. The combined filtrates were diluted with 3 liters of water and the small amount of precipitated matter filtered. From this precipitate was isolated 2.4 g. of Kerp's 9-fluorylacetylamine (according to Kuhn and Jacob $\gamma$-9-fluorylacetylamine). The filtrate was made strongly alkaline with aqueous ammonia. The amine which separated was dried (m. p. 60–61°) and precipitated as the hydrochloride from a benzene solution. The amine hydrochloride was recrystallized from dilute hydrochloric acid, from which it separated as long needles that melted with decomposition at 255°; yield 37 g. The free amine was obtained in the usual manner and recrystallized twice from hexane; m. p. 64–65°. Approximately 10 g. of 9-fluorylamine is soluble in 150 cc. of boiling hexane.

**Dibiphenyleneethane.**—This was prepared by heating a toluene solution of 9-chlorofluorene under reflux in the presence of copper powder. The recrystallized product melted at 247°.

**Reaction of 9-Fluorylamine with Dibiphenyleneethylene.**—Several preliminary qualitative experiments were carried out in liquid ammonia in order to determine the optimum conditions of the reaction. 9-Fluorylamine is appreciably soluble in liquid ammonia at room temperature. The solution, however, becomes pale green, probably due to some oxidation by a trace of oxygen. Dibiphenyleneethylene is somewhat soluble in liquid ammonia, imparting to it an orange-yellow color. The reaction between 9-fluorylamine and dibiphenyleneethylene is not photochemical and as one would expect is greatly accelerated by heat. As 9-fluorylamine is a weak base, a solution of its hydrochloride in liquid ammonia is just as effective as the free amine. Wet and sodium-dried liquid ammonia are equally satisfactory in carrying out the reaction of the amine with the ethylene compound.

A sealed tube containing 0.500 g. of 9-fluorylamine hydrochloride, 0.758 g. of dibiphenyleneethylene[11] and about 15 cc. of sodium-dried liquid ammonia was heated at a temperature of 40°. After heating for two hours an appreciable reaction had already taken place, as was shown by the appearance of long colorless prismatic needles. The

[9] Wieland and Roseeu, *Ann.*, **381**, 232 (1911).

[10] Kuhn and Jacob, *Ber.*, **58**, 1432 (1925).

[11] Wagner and Schmidt, *ibid.*, **43**, 1796 (1910). The hydrocarbon is best recrystallized from a solution of propyl and amyl alcohol.

reaction was practically completed in twenty-four hours. The progress of this reaction was followed by the gradual disappearance of the red ethylene compound.

After opening the tube, the ammonia was evaporated and the residue dried in a vacuum desiccator. The residue was then extracted with petroleum ether. The filtrate was allowed to evaporate in a desiccator containing paraffin. Pale yellow crystals separated that melted at 119°; mixed melting point with fluorenone imide[12] 122°. Further efforts to bring the imide to a higher state of purity were without success chiefly because of its sensitivity toward moisture. In order to confirm the fact that this substance was fluorenone imide, its ether solution was treated with dry hydrogen chloride. The orange-colored hydrochloride was precipitated; yield 0.45 g. It melted with decomposition at 265°; mixed decomposition point 268°. The hydrochloride was hydrolyzed by dissolving in water. The fluorenone was filtered, recrystallized from petroleum ether and melted at 83.5°; mixed m. p. with fluorenone unchanged.

The material insoluble in petroleum ether was treated with 10 cc. of hot toluene and filtered from the ammonium chloride. The toluene filtrate was concentrated to half of its original volume, diluted with an equal volume of ethyl alcohol, cooled and filtered; yield 0.54 g. Upon recrystallization it separated in beautiful white silky needles melting at 245°; mixed m. p. with dibiphenyleneethane, 245.5°.

No reaction was observed to take place when dibiphenyleneethylene and 9-fluorylamine were heated in such solvents as toluene, alcohol and pyridine.

**The Reaction of 9-Fluorylamine with Benzalfluorene.**—Upon heating the theoretical quantities of 9-fluorylamine and benzalfluorene[13] in liquid ammonia at 40° for one week, the reaction was found to be incomplete. For this reason the experiment was carried out at a higher temperature, using an excess of 9-fluorylamine.

A bomb tube containing 0.75 g. of 9-fluorylamine hydrochloride and 0.50 g. of benzalfluorene in liquid ammonia was heated at 60° for eight days. The tube was opened, the ammonia evaporated and the residue, a yellow oil, was dissolved in ether. The ether solution was treated with dry hydrogen chloride, which precipitated the hydrochlorides of fluorenone imide and 9-fluorylamine. The hydrochlorides, after filtering, were treated with water. The amine hydrochloride went into solution and the imide was hydrolyzed to fluorenone. The fluorenone was removed by filtration, recrystallized and identified; yield 0.055 g. Various attempts to separate benzylfluorene from benzalfluorene in the ether-soluble residue were unsuccessful.

**The Dehydrogenation of 9-Fluorylamine with Indigo.**—Since the completion of this reaction can be determined by the disappearance of the blue color of the solution, an excess of the amine was used. To a bomb tube containing wet liquid ammonia, was added 0.500 g. of 9-fluorylamine hydrochloride and 0.250 g. of indigo. The indigo was found to be insoluble at a temperature of −75°. However, it was sufficiently soluble at room temperature to give to the solvent a deep blue color. The reaction proceeded quite rapidly as in a few minutes the blue color of the solution had become greenish-yellow with the exception of a narrow band of blue at the surface of the liquid with a layer of a dark green color directly below. Upon shaking the tube more indigo went into solution, imparting to it a deep blue color, which again faded on standing, with the formation of the colored rings. This procedure was repeated several times, after which the rings at the surface were no longer formed. This phenomenon was without doubt due to the oxidation of the indigo white formed in the reaction by a slight amount of oxygen in the gaseous space of the tube. Upon shaking the tube in the latter stages of the experiment, the solution became dark green instead of blue,

[12] The preparation of fluorenone imide by treating fluorenone with liquid ammonia will be described in a later publication.

[13] Thiele, *Ber.*, **33**, 852 (1900).

indicating the presence of a considerable quantity of the yellow fluorenone imide. The bomb tube, after standing at room temperature for twenty-four hours, still contained a small amount of undissolved indigo. The reaction was then brought to completion by heating for fifteen minutes at 40°. The tube was opened and the indigo white oxidized to indigo by atmospheric oxygen. The ammonia was evaporated and the residue triturated with petroleum ether. The petroleum ether extract was treated with dry hydrogen chloride, which precipitated the hydrochlorides of fluorenone imide and 9-fluorylamine. The hydrochlorides were dissolved in water, which hydrolyzed the imide. The fluorenone was separated, purified and identified. The petroleum ether filtrate from the hydrochlorides was evaporated and yielded from 10–20 mg. of fluorene, the presence of which cannot be accounted for.

Another experiment was performed in which an excess of indigo was used. Here the fluorenone imide hydrochloride was obtained free from the amine hydrochloride and identified. The petroleum ether filtrate in this case did not contain any fluorene.

**The Reaction of 9-Fluorylamine with Methylene Blue.**—In one experiment 0.3 g. of 9-fluorylamine hydrochloride and 0.2 g. of methylene blue were treated with wet liquid ammonia. The solution turned a cherry red at room temperature and behaved similarly to the indigo experiment with regard to the fading of the dye in solution and the formation of the colored rings at the surface of the liquid. After one and one-half hours the reaction was complete and the solution was of a yellow color. The tube was opened and the leuco base oxidized to methylene blue. The imide and excess amine were precipitated as hydrochlorides and hydrolyzed; yield of fluorenone, 0.090 g. (theoretical, 0.113 g.).

**Reaction of 9-Fluorylamine with Azobenzene.**—Five-tenths of a gram of 9-fluorylamine hydrochloride and 0.42 g. of azobenzene dissolved completely in wet liquid ammonia at room temperature, producing a deep orange color. The reaction was carried out at a temperature of 40°. Within fifteen minutes an appreciable reaction had taken place, as was indicated by the decrease in intensity of the color of the solution. In thirty minutes the reaction was apparently complete, since on cooling the solution to about −75°, no azobenzene was precipitated. The tube was opened, the ammonia evaporated and the residue leached with ether. The ether filtrate was treated with dry hydrogen chloride and the precipitated hydrochlorides hydrolyzed. The fluorenone was separated (yield 0.360 g.), and after recrystallization melted at 82°; mixed melting point with an authentic specimen was unchanged.

The identification of hydrazobenzene was effected in another experiment in which the same quantities of reagents were used. The contents of the tube were transferred to a Dewar flask and the ammonia evaporated in a stream of nitrogen in order to prevent oxidation. The hydrazobenzene was rearranged to benzidine in the usual manner, filtered from fluorenone, precipitated first as the sulfate and then as the free base, which was identified; yield 0.16 g.

**Reaction of Hydrazobenzene with Dibiphenyleneethylene.**—A liquid ammonia solution containing 0.500 g. of dibiphenyleneethylene and 0.290 g. of hydrazobenzene was heated at 60° for a week. At the end of this time the reaction was complete. The progress of the reaction was easily followed by observing the gradual disappearance of the red ethylene compound, and the simultaneous increase in the colorless ethane. The tube was opened, the ammonia removed, the residue extracted with ether and filtered. The ether was removed from the filtrate and the red residue recrystallized from petroleum ether. The red needles (0.26 g.) which separated were shown to be azobenzene. The residue (0.28 g.) that was insoluble in ether was recrystallized twice from a solution of toluene and alcohol and melted at 247°; mixed m. p. with dibiphenyleneethane unchanged.

**Systems that Did Not Interact.**—The following products did not react under the conditions specified and in every case were recovered unchanged unless otherwise noted. In every case the solvent used was liquid ammonia.

(1) Tetraphenylethylene[14] and 9-fluorylamine were heated at 60° for twenty hours.

(2) Diphenylbiphenyleneethylene[15] and 9-fluorylamine hydrochloride heated at 40° for six days and then maintained at room temperature for one month.

(3) Stilbene and 9-fluorylamine hydrochloride, allowed to stand at room temperature for four months.

(4) Hydrazobenzene and 9-fluorylamine hydrochloride, heated at 60° for six days and kept at room temperature for three weeks.

(5) Benzhydrylamine and methylene blue, heated at 60° for three days and kept at room temperature for four days, benzophenone was not detected upon hydrolysis of the products.

(6) Dibiphenyleneethylene and benzhydrylamine, allowed to stand at room temperature for one month.

(7) Benzhydrylamine hydrochloride and indigo, heated at 60° for twelve days, the indigo was decomposed; however, no benzophene was obtained on hydrolysis of the products.

## Summary

1. Evidence has been obtained in favor of Wieland's theory of dehydrogenation as being one of the mechanisms of biological oxidation.

2. The dehydrogenation of 9-fluorylamine to fluorenone imide in liquid ammonia has been effected by dibiphenyleneethylene, benzalfluorene, azobenzene, indigo and methylene blue.

3. Dibiphenyleneethylene has been found to dehydrogenate hydrazobenzene to azobenzene.

[14] Schlenk and Bergmann, *Ann.*, **463**, 15 (1928).

[15] Kaufmann, *Ber.*, **29**, 75 (1896).

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE]

# THE ISOLATION OF CAROTENE

BY HARRY N. HOLMES AND HENRY M. LEICESTER

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Since von Euler,[1] von Euler and Karrer and T. Moore[2] showed that carotene can replace vitamin A in the diet of a rat suffering from a deficiency of this substance, the problem of obtaining the pigment with greater ease than formerly has become important. It seems certain that animals convert the carotene of plant food into vitamin A, hence the occurrence of the vitamin in butter, egg yolk and cod liver oil.

The methods used in the past[3] for the isolation of carotene have, in

[1] Von Euler, *Helv. Chim. Acta*, **12**, 278 (1929).

[2] Moore, *J. Soc. Chem. Ind.*, **49**, 238 (1930); *Biochem. J.*, **24**, 692(1930).

[3] For a summary of such methods, see Palmer, "Carotinoids and Related Pigments," The Chemical Catalog Co., New York, **1922**, Chap. 8.

general, been based upon the extraction of fresh carrots with a fat solvent, or with petroleum ether. In all of these processes, the carrot pulp has been dried for some time before extraction. Further, since a large quantity of carrots is necessary to obtain a relatively small amount of carotene, and since only a moderate amount can be worked up at a time in the average laboratory, many carrots must be left in the air with consequent loss of this valuable pigment by oxidation. In working with a substance as easily oxidized as carotene, exposure to air should obviously be avoided as much as possible, if good yields are to be obtained.

A study was therefore undertaken to develop a laboratory method for the isolation of carotene which would minimize the exposure of the materials to air at all times.

Determinations were first made upon a number of substances for their carotene content. The colorimetric method of Willstätter and Stoll as given by Palmer[4] was used and for the green leafy plants, the modification of Schertz was employed.[5] The results obtained are shown in Table I.

TABLE I

RESULTS OF DETERMINATIONS

| Source | Carotene, mg. per 100 g. | Xanthophyll, mg. per 100 g. |
|---|---|---|
| Alfalfa (cured) | 2.3 | 9.0 |
| Dehydrated spinach | 1.5 | 3.9 |
| Fresh spinach | 4.8 | 8.6 |
| Canned spinach (drained) | 15.6 | 16.1 |
| Yellow corn gluten | 0.3 | ... |
| Canned carrots (drained) | 6.5 | ... |

These results show that dehydrated spinach and alfalfa have lost most of their carotene during drying. The low value for fresh spinach is surprising, and may be due to the fact that, as the vegetable was purchased on the open market, it may have been exposed to the air for some time. Also, since it was winter grown spinach, it may have had less sun and hence formed less pigment. The yellow corn gluten (a commercial stock food) is surprisingly low in the pigment, while canned spinach and canned carrots are relatively rich in this substance.

In view of these findings, the study was begun on the green, leafy plants. A method of treatment was developed which did away with the necessity of separating all the pigments together, and then removing the chlorophyll, as has previously been done. This improved method consists in permitting the green leaf to stand for three hours with enough 3 *N* sodium hydroxide to form a thick paste. This disintegrates the cellulose and hydrolyzes the chlorophyll to water-soluble chlorophyllines, but does not injure the carotenoids. The mixture is then diluted with an equal volume of water, and

[4] Palmer, Ref. 3, pp. 259–260.

[5] Schertz, *Plant Physiol.*, **3**, 211 (1928).

the whole mass is extracted with chloroform, taking care not to agitate to such an extent that troublesome emulsions result. The heavy solvent sinks to the bottom of a separatory funnel, and can easily be drawn off.

In this way a deep red solution of carotene and xanthophyll in chloroform uncontaminated by any chlorophyll can be obtained in a short time. Evaporation of the solvent leaves a fatty, orange mass. This can be dissolved in petroleum ether, and the usual separation of carotene and xanthophyll, by extracting the xanthophyll with 80–90% methyl alcohol, can be carried out.[6]

This method appears to be advantageous if a solution of carotenoids is desired for study, since it is rapid and the pigments are not mixed with other colored substances. It may also be used when the isolation of mixed carotene and xanthophyll is intended. However, the removal is not quite quantitative, and the subsequent treatment required to isolate carotene is troublesome for the average laboratory, if large amounts are desired. On a commercial basis this method seems attractive.

Therefore, it appeared best to turn again to carrots, long the principal source of the pigment. As shown in Table I, they do not contain as much of this substance as spinach, but they contain no interfering pigments, and the extraction is a relatively straightforward process.

The value of canned carrots as a laboratory source of carotene appears heretofore to have been overlooked. However, there are many striking advantages in their use. The carrots have been cooked very soon after picking, and in hermetically sealed containers. This eliminates almost all opportunities for oxidation to occur. The carrots thus prepared can be kept on hand indefinitely, and used only as convenient, without deterioration of the pigment. They are soft and easily crushed and worked up.

It is obvious that the same advantages apply to canned spinach as a source of carotene and xanthophyll.

The carrots employed were the Huxon Brand Diced Carrots, obtained in one gallon cans. The weight of solid in these cans ranged from 1800 to 2000 g. after the juice had been drained off. It was found convenient to work up four cans at a time.

The first step was to crush the carrots in a Carver Hydraulic Hand Press. A pressure of 8000 pounds to the square inch was sufficient to squeeze out almost all the juice. The two kilograms of carrots in a can were thus reduced to a weight of about 330 g. The juice pressed out contained practically no carotene and was discarded.

The press cake from four cans was ground up in a meat grinder and placed under 1.25 liters of acetone. After standing thus from eight to ten hours, the mixture was filtered on a Büchner funnel, and the pulp pressed once more, again with a pressure of 8000 lbs. per sq. in. This removed the remaining traces of water and permitted the later use of water-insoluble solvents for removal of carotene. This method of dehydra-

[6] Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, Inc., New York, 1927, p. 309.

## TABLE I

### COMPARISON OF VARIOUS METHODS OF ISOLATING CAROTENE FROM CARROTS

| Holmes and Leicester, 1931 | Arnaud, 1886 | Kohl, 1902 | Euler and Nordenson, 1908 | Escher, 1909 | Strain, 1931 | Guthrie, 1929 |
|---|---|---|---|---|---|---|
| Canned carrots | Fresh carrots | Fresh carrots | Fresh carrots | Fresh carrots | Fresh carrots | Fresh carrots |
| | Grate | Boil | Boil | Dry at low heat | Dry rapidly | |
| Press | Press | Press | Press | | | |
| | Add $Pb(Ac)_2$ to juice | | | | | |
| | Filter ppt. | | | | | |
| Grind | | | Grind with sand | Grind | Grind | Grind |
| Wash with acetone | | Wash with alcohol | | | | Wash 2 times with acetone |
| Filter, press | | Filter, press | | | | |
| Grind | | Grind | | | | |
| | Dry ppt. and pulp *in vacuo* | Dry in air | Dry at 50° air | | | |
| | | | Extract twice with $CS_2$ | | | |
| | | | Press | | | |
| | | | Distil off $CS_2$ with ether | | | |
| Extract with acetone, pet. ether | Extract with $CS_2$ | Extract with ether in cont. extractor | Extract pulp with alcohol | Extract with pet. ether in cont. extractor | Extract with pet. ether | Extract 3 times with acetone |
| Transfer pigment to pet. ether | | | Transfer pigment to ether | | | |
| | | | Evap. all ether | | | |
| | | | Dissolve residue in pet. ether | | | |
| Conc. pet. ether | Conc. $CS_2$ soln. | Conc. ether | | Conc. pet. ether | Conc. pet. ether | Add 1/3 volume $H_2O$ and allow to crystallize |
| Add alc., filter | | | Add alc., filter | | | |
| Carotene cryst. | Crude carotene crystallizes | Crude carotene crystallizes | Carotene cryst. | Crude carotene crystallizes | Carotene crystallizes at 5° | |

tion eliminated the necessity of air drying and the inevitable loss by oxidation. Guthrie[7] has also dehydrated carrots in a similar way.

The pulp, now a solid cake, was reground and allowed to stand for half an hour with 1.25 liters of fresh acetone. It was then filtered as before, and placed under one liter of petroleum ether. After an hour this solvent was filtered off and replaced by a liter of acetone. This also was allowed to stand for an hour, then was filtered and a final liter of petroleum ether was placed on the carrots. After another hour they were filtered and washed with 0.5 to 0.75 liter of petroleum ether. The pulp was then practically colorless, and further extraction was unnecessary. This alternation of solvents was used because it was found that less total volume of solvent had to be employed than if either had been used alone. Also, by dissolving the acetone extracts in the petroleum ether and washing the solvent out with water, the pigment it carried was transferred to the latter solvent, and less time was consumed during evaporation. The continuous extraction process might well be used on a commercial scale.

The petroleum ether was evaporated to about 75–100 cc. under reduced pressure, and then treated with a large excess of absolute alcohol, with violent stirring. A fatty substance precipitated and settled out. This was rapidly filtered off, the filtrate was placed in a flask in an atmosphere of nitrogen, and was allowed to stand for twenty-four hours in the ice box. The carotene crystallized out in dark red lustrous crystals.

From 100 gallons of canned carrots a quantity of carotene was obtained which, after standing over phosphorus pentoxide in a vacuum desiccator to remove solvent of crystallization, weighed 7.5 g. This is a yield of approximately 0.037 g. of pigment per kilogram of carrots, and compares very well with the yield of 0.025 g. per kilo obtained by Escher[8] and of 0.030 g. per kilo obtained by Arnaud.[9] After four precipitations from chloroform by methyl alcohol as recommended by Olcovitch and Matill,[10] the carotene melted at 173.6–174.6° (corr.).

## Summary

1. The carotene content of several vegetables has been determined.

2. A rapid yet cheaper method for obtaining a solution of carotene and xanthophyll free from chlorophyll has been described.

3. The advantages of canned vegetables as sources of carotenoids have been pointed out.

4. A modified method for the cheaper isolation of carotene in good yield from canned carrots has been described.

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[7] Guthrie, *Am. J. Bot.*, **16**, 716 (1929).

[8] *Cf.* Palmer, Ref. 3, p. 201.

[9] Arnaud, *Compt. rend.*, **102**, 1119 (1886).

[10] Olcovitch and Matill, *J. Biol. Chem.*, **91**, 105 (1931).

[CONTRIBUTION FROM THE SCHOOL OF ENGINEERING RESEARCH, UNIVERSITY OF TORONTO]

# A STUDY OF CERTAIN PROPERTIES AND REACTIONS OF PHENYLHYDRAZINE

BY E. G. R. ARDAGH,[1] B. KELLAM, F. C. RUTHERFORD AND H. T. WALSTAFF

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## Part I

**Determination of Phenylhydrazine.**—The need for a simple and dependable method for the quantitative determination of phenylhydrazine arose as a result of the use of this reagent by Ardagh and Williams[2] in the quantitative determination of the carbonyl group in organic compounds. The present paper should be read in conjunction with the two just referred to, since it is impossible, due to lack of space, to repeat much of the detail given there.

In the quantitative determination of acetophenone and benzophenone we employed ethyl alcohol + water as solvent for these ketones since they are too sparingly soluble in water alone for practical purposes.

The method recommended by Ardagh and Williams for the determination of phenylhydrazine[2] by titration with iodine in slightly acid solution, the course of which reaction is represented by the equation given at the end of this paragraph, gives low results when more than 10% by volume of alcohol is present. This is particularly the case when the phenylhydrazine is very dilute, say, 0.01 *M*.

$$C_6H_5HN{\cdot}NH_2 + 2I_2 \longrightarrow C_6H_5I + 3HI + N_2$$

To accelerate the rate of the reaction between the ketone and the phenylhydrazine, heating the mixture to 60° under an atmosphere of nitrogen is very effective. At this temperature some phenylhydrazine is always destroyed when alcohol is present even in solutions as acid as *P*H 2, but if the *P*H does not exceed 4 the destruction of phenylhydrazine is reduced practically to a constant (about 2% of the amount present after heating to 60° for three hours, and 5% for nine hours) even though the alcohol present may make up half the total volume, as shown in the accompanying graph (Fig. 1).

The effects of considerable quantities of alcohol on the figures obtained for phenylhydrazine may be summed up as follows.

(1) On heating the solution containing the phenylhydrazine to 60° for three hours, the decomposition of phenylhydrazine in faintly acid solution (*P*H about 4) is independent of the proportion of alcohol present and is roughly a constant at 2% of the amount of phenylhydrazine present. It is most important that the alcohol be free from aldehydes and traces of

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[2] Ardagh and Williams, THIS JOURNAL, 47, 2976, 2983 (1925).

other impurities which will react with iodine. Sometimes absolute alcohol is prepared by the use of calcium carbide. In this case traces of acetylene will be present.

(2) When alcohol and buffer are both present (we used $NaH_2PO_4$), numerous factors appear to affect the iodine–phenylhydrazine reaction, *e. g.*, rate of addition of iodine, excess of reagents, time allowed for reaction, etc.

(3) When alcohol without buffer is present, the titration gives more trouble than when buffer without alcohol is present, but either is less uncertain than when both alcohol and buffer are present.

(4) The phenylhydrazine content of the solution to be titrated should not fall below approximately 0.05 *M*, especially if alcohol is present.

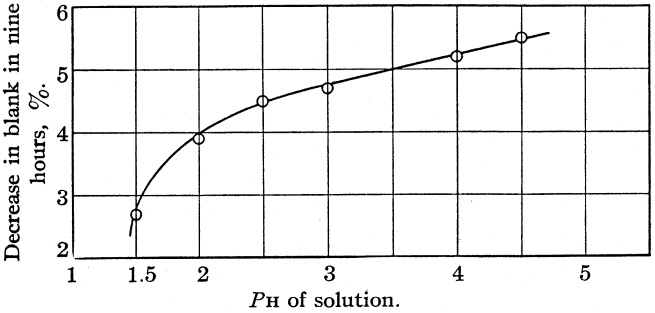


Fig. 1.—Change in phenylhydrazine value with PH of solution of $C_6H_5NHNH_2 \cdot HCl$ heated for nine hours at 60° (50% alcohol).

(5) The phenylhydrazine solution should be added to an excess of the standard iodine and the mixture allowed to stand for five minutes before titrating the excess iodine.

(6) When alcohol is present the end-point is improved by adding 2 to 3 cc. of thiosulfate in excess and shaking gently to remove the iodine dissolved in the droplets of iodobenzene. If these droplets are very minute a more certain end-point is secured by omitting the ether formerly recommended.[2]

Owing to the inconvenience as well as the instability of the phenylhydrazine base, we prepared the hydrochloride, which we used in all our work. To obtain the salt free from impurity, the base, after redistilling at 16 mm. under nitrogen followed by diluting with alcohol, must be added slowly with constant stirring to an excess of the acid, also diluted with alcohol. If the reverse method is followed a product containing aniline hydrochloride and even ammonium chloride is likely to be obtained as a result of the reaction shown here, especially if the mixture is allowed to become warm.[3]

$$2C_6H_5HN \cdot NH_2 + C_6H_5HNNH_2 \cdot HCl \longrightarrow 3C_6H_5NH_2 + NH_4Cl + N_2$$

[3] M. Busch, *J. prakt. Chem.*, **116**, 39 (1927).

Proceeding in the manner described we had no difficulty in preparing beautiful, lustrous, white scales of the hydrochloride which, after washing, first with alcohol, then with diethyl ether, and drying to constant weight over porous calcium chloride in a desiccator filled with nitrogen, required for titration the precise proportion of 0.1 *N* iodine calculated for the pure salt.

Experiment proved that 25 cc. of a 0.25 *M* solution in water of the hydrochloride diluted to 100 cc. when exposed to air turned brown and turbid in a few days, as a result of oxidation.

In our attempts to find an inhibitor against oxidation we tried adding 0.1 g. of each of the following to 100 cc. batches of the above: pyridine, quinoline, *o*-toluidine, *m*-phenylenediamine and β-naphthylamine. None of these appeared to exercise any inhibitory effect. The addition of 0.5 cc. of 6 *N* hydrochloric acid to a 100-cc. batch appeared, on the contrary to be most effective. Doubtless this was due to the resulting increase in hydrogen-ion concentration.

In our work we preferred to prepare our phenylhydrazine solutions from day to day from the pure, dry hydrochloride. This practice we considered to be more free from possible sources of error than any other method.

## Part II

$$C_6H_5CH_3C{=}O + C_6H_5HNNH_2{\cdot}HCl \rightleftharpoons C_6H_5CH_3C{=}NNHC_6H_5 + HCl + H_2O$$

**Optimum Conditions for the Preparation of Acetophenone Phenylhydrazone.**—In the earlier work referred to, the authors' object was the development of an analytical method for the quantitative determination of aldehydes and ketones; in Part II and Part III of the present article the purpose is to discover the conditions that will result in a high yield of hydrazone in a short time.

Ardagh and Williams found that the conditions necessary to give a high percentage yield of hydrazone in a reasonable time from acetophenone and from benzophenone must be maintained within narrower limits than are required in the case of the aldehydes and ketones of the aliphatic series, and furthermore that the rate of hydrazone formation is too slow at room temperature to be satisfactory. This is particularly the case with benzophenone.[4]

At 60° the reaction proceeds much more rapidly. The hydrogen-ion concentration of the solution, as one would expect, also has an important influence upon the rate.

The accompanying graph (Fig. 2) constructed from our results shows the effect of the hydrogen-ion concentration upon the rate of the formation of acetophenone phenylhydrazone at 60°. The optimum $P_H$ evidently lies between the limits 4 and 5.

The following method we found to be very successful.

[4] Ref. 2, p. 2988.

To a 100-cc. ground-glass stoppered graduated flask were added 25 cc. of 0.25 *M* $C_6H_5HNNH_2 \cdot HCl$, 25 cc. of buffer solution (0.5 *M* $NaH_2PO_4$), to which enough phosphoric acid had been added to give the buffer a $P_H$ of 4.6, 10 cc. of acetophenone (1 cc. contained 0.0246 g. of acetophenone) dissolved in 40% alcohol by volume and 40 cc. of sodium chloride containing 370 g. per liter (saturated). The air was displaced by nitrogen and the tightly stoppered flask immersed in a water-bath at 60°. The yield was 100% of the theoretical in less than thirty minutes. The time required to obtain 100% yield at room temperature as shown in graph V was twelve hours in a solution having a $P_H$ of 6.1. No doubt the time required would have been materially reduced if the $P_H$ had been adjusted to between 4 and 5.

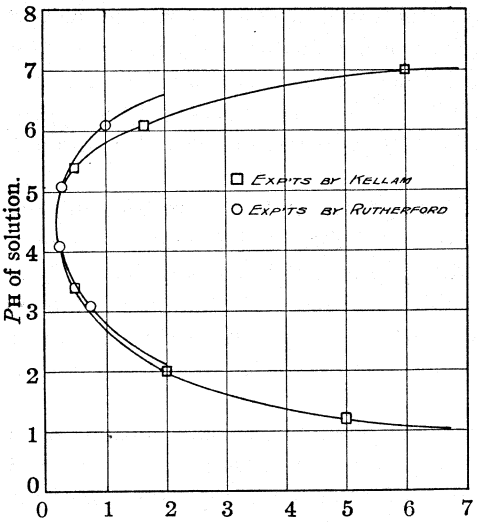


Fig. 2.—Relation between $P_H$ of solution and time required to produce 100% yield of acetophenone phenylhydrazone.

Figures 3 and 4 show the rate of reaction at 60° at a $P_H$ of 7.0 and of 7.8, respectively. These rates are quite obviously very much slower than for lower $P_H$'s. In fact it is possible that at $P_H$ 7.8 the reaction might never arrive at completion.

All the determinations of phenylhydrazine were made by the method described in the earlier paper referred to,[5] with such modifications as have herein been shown to be necessary in the presence of alcohol.

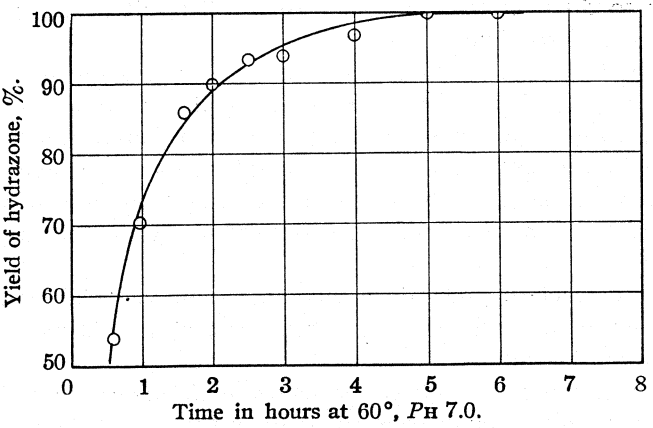


Fig. 3.—Acetophenone phenylhydrazone, time–yield, $P_H$ 7.0.

In each determination we added 10 cc. of the phenylhydrazine solution to an excess of the 0.1 *N* iodine, usually 30 cc.

[5] Ref. 2, p. 2986.

## Part III

$$(C_6H_5)_2C{=}O + C_6H_5HNNH_2{\cdot}HCl \rightleftharpoons (C_6H_5)_2C{=}NNHC_6H_5 + HCl + H_2O$$

**Optimum Conditions for the Preparation of Benzophenone Phenylhydrazone.**—To secure 100% yield of this hydrazone from the ketone in a reasonable time necessitates very careful control of conditions. To keep

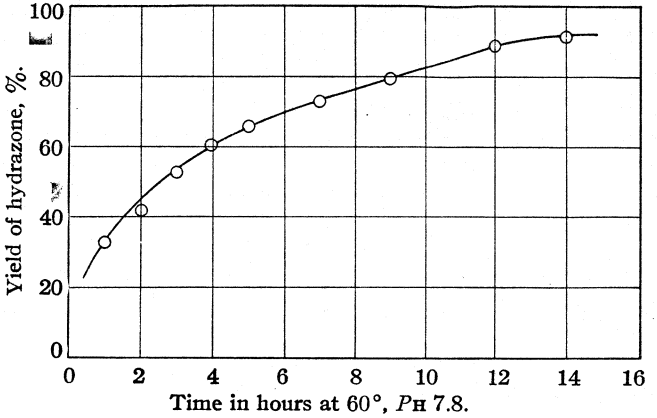


Fig. 4.—Acetophenone phenylhydrazone, time–yield, $P_H$ 7.8.

the ketone in solution, the alcoholic content of the mixture must be not much below 50% by volume. Even at 60° and with 50% alcohol the reaction proceeds much more slowly than for acetophenone.

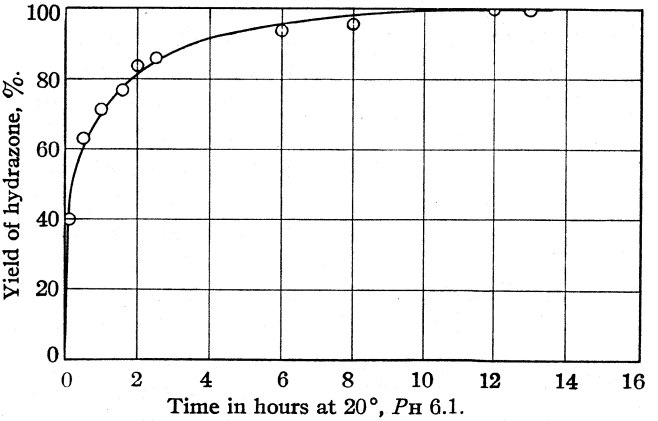


Fig. 5.—Acetophenone phenylhydrazone, time–yield, $P_H$ 6.1.

In the formation of the hydrazone, water is split off. One would expect, therefore, that by using absolute alcohol the rate of reaction would rise. The solubility of the hydrazone would, however, increase with increase in alcohol concentration. As a result the yield of hydrazone would tend to

diminish above a certain alcoholic concentration in spite of the increase in the rate of its formation. We had not time to determine experimentally,

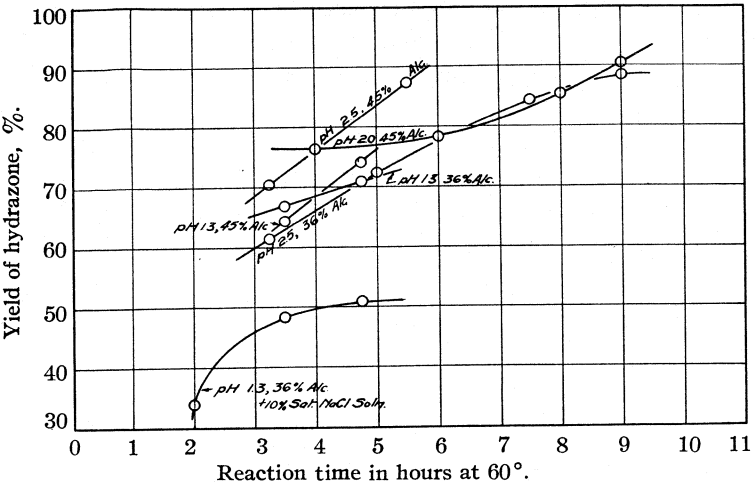


Fig. 6.—Yields of benzophenone phenylhydrazone in solutions of different composition, %.

from the viewpoint of both time and yield, the most effective alcoholic concentration. In any case the opinion of the experimenter would also have an important bearing upon the interpretation of the word *effective*. An increase in alcohol content would, unfortunately, add to our analytical troubles, and since the study was originally undertaken for the purpose of developing an analytical method, we have endeavored for this reason to keep the alcohol concentration down to a convenient figure. Figure 6 gives some indication of the influence at 60° of the hydrogen-ion concentration and of the alcoholic content upon the rate of the reaction.

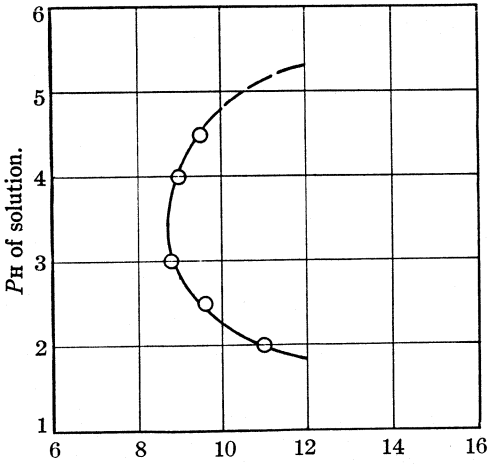


Fig. 7.—Relation between $P_H$ of solution (50% alcohol) and time required to produce 100% yield of benzophenone phenylhydrazone.

Figure 7 shows the effect of the hydrogen-ion concentration on the rate of the reaction at 60° when the alcoholic content of the solution is 50% by volume. The optimum hydrogen-ion concentration evidently

lies between $P_H$ 3 and 4, which is very close to the hydrogen-ion concentration of 0.25 $M$ phenylhydrazine hydrochloride itself ($P_H$ 3.5).

It seems strange that the addition of saturated sodium chloride retards the rate of formation of this hydrazone, since in all the other hydrazones we prepared the reverse is the case.

One peculiar phenomenon observed in dealing with both the acetophenone and benzophenone phenylhydrazones was that, while both hydrazones are capable of supersaturation to a high degree during formation, nevertheless when they were forced out of solution as soon as they were formed (by constant agitation) the rate of formation was not increased. In the case of the benzophenone phenylhydrazone it even seemed that the longer the elapsed time before the crystals of hydrazone appeared (depending on the menstruum employed), the higher was the final yield.

## Summary

1. The conditions requisite for obtaining satisfactory results in the iodimetric determination, more particularly in the presence of ethyl alcohol, have been worked out.

2. The effect of hydrogen-ion concentration upon the minimum time required to secure a high yield of the hydrazones of acetophenone and benzophenone has been determined.

3. Details of a method by which very pure phenylhydrazine hydrochloride can be prepared have been worked out.

TORONTO, CANADA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# RESEARCHES ON PYRIMIDINES. CXXIII. THE REARRANGEMENT OF 2,6-DIMETHOXY-4-CHLOROPYRIMIDINE AND 2,4,6-TRIMETHOXYPYRIMIDINE IN THE PRESENCE OF METHYL IODIDE[1]

BY HARRY J. FISHER AND TREAT B. JOHNSON

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Hilbert and Johnson[2] showed that 2,6-dimethoxypyrimidine I in the presence of methyl iodide was quantitatively rearranged at room temperature to 2-oxy-3-methyl-6-methoxypyrimidine III.

$$\underset{\text{I}}{\overbrace{N{=}C(OCH_3){-}N{=}C(OCH_3)CH{=}CH}} + CH_3I \longrightarrow$$

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[1] This paper is constructed from a portion of a Dissertation presented by Harry Johnstone Fisher to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[2] Hilbert and Johnson, THIS JOURNAL, **52**, 2001 (1930); Johnson and Hilbert, *Science*, **69**, 579 (1929).

$$CH_3N{=}C(OCH_3)N{=}C(OCH_3){-}CH{=}CH \longrightarrow$$

II

$$CH_3I + CH_3NCON{=}C(OCH_3)CH{=}CH$$

III

While the intermediate compound II was not isolated, evidence that the above equations represent the mechanism of the reaction was afforded by the behavior of 2,6-diethoxypyrimidine with methyl iodide. In this case the reaction product was 2-oxy-3-methyl-6-ethoxypyrimidine.

When acetobromoglucose was substituted for methyl iodide, it was found possible to prepare a nucleoside derivative of uracil with the sugar attached to the nitrogen in position 3.[3] Schmidt-Nickels and Johnson[4] later showed that 2,6-dimethoxy-5-methylpyrimidine IV and 2,6-diethoxy-5-methylpyrimidine V likewise rearranged quantitatively in the presence of methyl iodide at room temperature, giving, respectively, 2-oxy-3,5-dimethyl-6-methoxypyrimidine VI and 2-oxy-3,5-dimethyl-6-ethoxypyrimidine VII. Analogous transformations were obtained in the presence of ethyl iodide.

$$N{=}C(OCH_3){-}N{=}C(OCH_3){-}C(CH_3){=}CH \longrightarrow$$

IV

$$CH_3N{-}CO{-}N{=}C(OCH_3){-}C(CH_3){=}CH$$

VI

$$N{=}C(OC_2H_5){-}N{=}C(OC_2H_5){-}C(CH_3){=}CH \longrightarrow$$

V

$$CH_3N{-}CO{-}N{=}C(OC_2H_5){-}C(CH_3){=}CH$$

VII

The present study was undertaken with the ultimate aim of synthesizing barbituric acid 3-glucoside. With this end in view, the behavior of 2,6-dimethoxy-4-chloropyrimidine VIII and 2,4,6-trimethoxypyrimidine IX toward methyl iodide was investigated.

$$N{=}C(OCH_3){-}N{=}C(OCH_3){-}CH{=}CCl$$

VIII

$$N{=}C(OCH_3){-}N{=}C(OCH_3){-}CH{=}C(OCH_3)$$

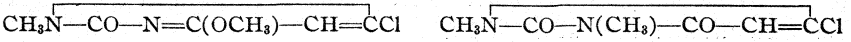
IX

It was found that VIII, in contrast to the behavior of I, IV and V, did not rearrange at all when dissolved in methyl iodide and allowed to stand at room temperature, nor was there any reaction at the boiling point of methyl iodide. When VIII was heated with methyl iodide, in a sealed

[3] Hilbert and Johnson, THIS JOURNAL, **52**, 4489 (1930); Johnson and Hilbert, *Science*, **69**, 579 (1929).

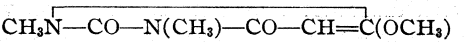
[4] Schmidt-Nickels and Johnson, THIS JOURNAL, **52**, 4511 (1930); Johnson, *Ber.*, **63**, 1974 (1930).

tube at 100°, rearrangement did take place, but the change was not quantitative, and the reaction product was not the partially rearranged pyrimidine X, but 1,3-dimethyl-4-chlorouracil XI. In other words, when rearrangement did take place the completely rearranged pyrimidine resulted.

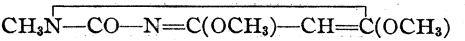


X XI

Trimethoxypyrimidine IX did react with methyl iodide at room temperature, and more readily at 60°. Here likewise the completely rearranged 1,3-dimethyl-4-methoxyuracil XII was formed, but also the partially rearranged compound, 2-oxy-3-methyl-4,6-dimethoxypyrimidine, XIII.



XII



XIII

The inability of VIII to rearrange at room temperature as did the compounds studied by Hilbert and Johnson and Schmidt-Nickels and Johnson is believed to be due to the decreased basicity caused by the presence of a chlorine atom in position 4 of the pyrimidine cycle with a consequent lessened tendency toward the formation of the intermediate quaternary compound with methyl iodide. That VIII is less basic than IX, which does react with methyl iodide at room temperature, is shown by the fact that IX dissolves readily in dilute hydrochloric acid and forms a compound with gold chloride,[5] while VIII is apparently no more soluble in hydrochloric acid than in water. Chapman[6] in his study of the rearrangement of N-arylaminoaryl ethers to acyl diphenylamines noted that the presence of negative substituents in the amino group retarded the change.

The explanation of the formation of the completely rearranged compounds in the reactions of VIII and IX with methyl iodide, instead of the partially rearranged compounds obtained quantitatively from I, IV and V, under the same conditions, probably lies in the difference in the solubility relations of the compounds involved. 2,6-Dimethoxypyrimidine I is a liquid at ordinary temperatures, readily miscible with methyl iodide, while 2-oxy-3-methyl-6-methoxypyrimidine III is a solid melting at 150°, which crystallizes out of the reaction mixture as formed, and so is removed from the action of the methyl iodide before further rearrangement takes place. In the case of the reaction of IX with methyl iodide, the partially rearranged compound XIII has a melting point of only 97°, and at the temperature of the reaction (60°) probably remains largely dissolved in the

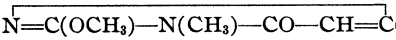
[5] Büttner, *Ber.*, **36**, 2227 (1903).

[6] Chapman, *J. Chem. Soc.*, 569 (1929).

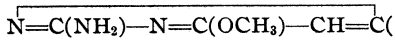
methyl iodide and so undergoes further rearrangement to XII. As compound X has not been isolated, its melting point is unknown, but it may be speculated that the same explanation holds for the formation of the completely rearranged compound in the reaction of VIII with methyl iodide, particularly as this rearrangement was carried out at the comparatively elevated temperature of 100°.

The constitution of 1,3-dimethyl-4-chlorouracil XI, which has not previously been described, was established by hydrolyzing it to 1,3-dimethylbarbituric acid by evaporation with concentrated hydrochloric acid on the steam-bath.

Of the rearrangement products of IX, 1,3-dimethyl-4-methoxyuracil XII has been prepared by Biltz and Wittek[7] and by Herzig[8] by methylating barbituric acid with diazomethane. Its constitution was also proved by hydrolysis to 1,3-dimethylbarbituric acid with hydrochloric acid. 2-Oxy-3-methyl-4-6-dimethoxypyrimidine XIII has not been previously isolated in pure form, although Herzig found in the mother liquors from his preparation of XII a substance analyzing for two methoxyl groups, melting at 75–90°, which he was unable to purify, that may have been this compound. The partially rearranged compound obtained from the reaction of IX with methyl iodide yielded 1-methylbarbituric acid on hydrolysis with hydrochloric acid, and on the basis of this evidence the constitution XIII has been assigned to it. While the compound of structure XIV would likewise give 1-methylbarbituric acid, from the evidence of the work of Hilbert and Johnson and Schmidt-Nickels and Johnson the methyl group shifts first to the 3-position, so formula XIII appears the most reasonable.



XIV



XV

In the course of the study of the rearrangement of the alkoxy pyrimidines, 2-amino-4,6-dimethoxypyrimidine XV was prepared. It is a solid melting at 95°.

## Experimental Part

**2,6-Dimethoxy-4-chloropyrimidine.**—This compound was prepared by Büttner[5] from trichloropyrimidine in two steps. It was found that it could be made directly from trichloropyrimidine.

Twenty-five grams of trichloropyrimidine (prepared from barbituric acid by the method of Gabriel and Colman)[9] in 360 cc. of absolute methanol was mixed with a solution of 6.4 g. of sodium in 81 cc. of methanol and let stand overnight. The next day the solution was decanted from sodium chloride, cooled in ice and the crystals which

[7] Biltz and Wittek, *Ber.*, **54**, 1035 (1921).

[8] Herzig, *Z. physiol. Chem.*, **117**, 13 (1921).

[9] Gabriel, *Ber.*, **33**, 3666 (1900); Gabriel and Colman, *ibid.*, **37**, 3657 (1904).

separated filtered and washed with water. The sodium chloride was dissolved in a little water, the solution cooled and the crystals separating filtered, washed, combined with the first crop and dried in vacuo; yield, about 13 g.

Recrystallized from petroleum ether, ethyl alcohol or methyl iodide the substance melts at 76–77°. Slow crystallization from methyl iodide yields perfectly formed prisms several millimeters long.

**2,4,6-Trimethoxypyrimidine.**—Büttner[5] prepared this compound by heating trichloropyrimidine in a sealed tube at 100°. It was found that the third chlorine atom could be removed by a less drastic treatment.

Thirty grams of trichloropyrimidine in 240 cc. of absolute methanol was mixed with a solution of 23 g. of sodium in 290 cc. of methanol, the mixture refluxed for one hour and let stand overnight. The solution was decanted from the sodium chloride, mixed with 330 cc. of water and cooled in ice. The colorless needles which crystallized out were filtered, washed with a little water and dried in vacuo.

The sodium chloride was dissolved in water, cooled in the ice-box overnight, and the long needles which crystallized out in very pure condition were filtered, washed with water and dried in a desiccator. The total yield was about 19 g. Trimethoxypyrimidine separates in long silky needles which are usually quite pure and melt at 57°. It can be recrystallized best from dilute methanol.

*Anal.* Calcd. for $C_7H_{10}O_3N_2$: N, 16.47. Found: N, 16.73.

**The Action of Methyl Iodide on 2,6-Dimethoxy-4-chloropyrimidine.**—When 2,6-dimethoxy-4-chloropyrimidine was refluxed for six and one-half hours with sufficient methyl iodide to dissolve it, the mixture allowed to stand overnight and the methyl iodide evaporated on the water-bath, a crystalline residue was left which melted at 70–75° without purification, and after one recrystallization from petroleum ether melted at 77°. A mixed melting point with the original substance showed no depression.

When the temperature was raised to 100° reaction took place. Five grams of 2,6-dimethoxy-4-chloropyrimidine and 10 g. of methyl iodide were heated at 100° in a sealed tube for thirty hours and the tube allowed to stand without opening for thirty-nine days. The contents of the tube were then evaporated on the water-bath, the pasty residue extracted with a little ether and the light-colored residue recrystallized from alcohol after decolorization by the use of norite. 1,3-Dimethyl-4-chlorouracil crystallized in colorless prisms melting at 111°. The yield was about 3 g.

*Anal.* Calcd. for $C_6H_7O_2N_2Cl$: N, 16.06. Found: N, 16.21, 15.96.

When this pyrimidine was mixed with concentrated hydrochloric acid and the mixture evaporated to dryness on the steam-bath, the residue on recrystallization from alcohol gave colorless needles melting at 121–122°. A mixed melting point with a sample of 1,3-dimethylbarbituric acid, prepared by the method of Techow[10] from tetramethyl alloxantin which had been obtained from caffeine by the procedure of Biltz,[11] showed no depression.

*Anal.* Calcd. for $C_6H_8O_3N_2$: N, 17.95. Found: N, 17.93, 17.93.

**The Action of Methyl Iodide on 2,4,6-Trimethoxypyrimidine.**—When 2,4,6-trimethoxypyrimidine was dissolved in three times its weight of methyl iodide and allowed to stand at room temperature, there was no visible change in twenty-four hours. Nevertheless, on working up the reaction mixture, some 1,3-dimethyl-4-methoxyuracil XII was found. On standing for a week the mixture, which had gradually grown darker, began to deposit crystals of XII. At the end of a month the reaction mixture was filled with crystals of XII, the amount being about 60% of the original material.

[10] Techow, *Ber.*, **27**, 3082 (1894).

[11] Biltz, *ibid.*, **45**, 3674 (1912).

Ten grams of trimethoxypyrimidine and 20 g. of methyl iodide were heated in a sealed tube at 60° for forty-eight hours. On cooling a large amount of crystals was deposited from the dark red liquid. Without separation, the contents of the tube were evaporated on the steam-bath, the residue taken up in 20 cc. of chloroform, 80 cc. of petroleum ether added, the mixture cooled in ice and the dark red precipitate filtered and washed with petroleum ether. Heated for half an hour at 125° the residue became nearly colorless; wt., 5 g. Recrystallized from benzene, the 1,3-dimethyl-4-methoxyuracil was obtained in long colorless needles melting at 164–166°.

*Anal.* Calcd. for $C_7H_{10}O_3N_2$: N, 16.47. Found: N, 16.68.

A mixed melting point with a sample of XII prepared from barbituric acid and diazomethane by the method of Biltz and Wittek[7] showed no depression. Hydrolysis with hydrochloric acid yielded 1,3-dimethylbarbituric acid.

The chloroform–petroleum ether solution from which XII had precipitated was evaporated. The light yellow residue after several recrystallizations from ether melted at 95.5–97°.

*Anal.* Calcd. for $C_7H_{10}O_3N_2$: N, 16.47. Found: N, 16.73.

This substance on evaporation with concentrated hydrochloric acid and recrystallization of the residue from alcohol gave needles melting at 132°, which showed no depression in melting point when mixed with 1-methylbarbituric acid prepared by the method of Biltz and Wittek.[7]

*Anal.* Calcd. for $C_5H_6O_3N_2$: N, 19.72. Found: N, 20.31.

On the basis of this evidence it was concluded that the substance was 2-oxy-3-methyl-4,6-dimethoxypyrimidine.

**The Preparation of 2-Amino-4,6-dimethoxypyrimidine.**—2-Amino-4,6-dichloropyrimidine was prepared by the method of Büttner[5] from malonylguanidine made from guanidine thiocyanate and malonic ester according to Michael.[12] The dried crude product was used without the purification by vacuum sublimation recommended by Büttner.

Five grams of crude 2-amino-4,6-dichloropyrimidine, 14 cc. of an absolute methyl alcoholic solution of 1.2 g. of sodium and 136 cc. of absolute methanol were heated in a pressure-bottle in steam for four hours, then let stand overnight. The mixture was then distilled in vacuo to a small volume, diluted with water and extracted with ether. The ether extract was dried with calcium chloride, filtered and the ether evaporated. The residue was a light yellow oil which solidified on cooling; wt. about 3 g. Recrystallized from ligroin, it separated in colorless prisms melting at 95°. A test for chlorine was negative.

*Anal.* Calcd. for $C_6H_8O_2N_3$: N, 27.09. Found: N, 26.93.

## Summary

1. 2,6-Dimethoxy-4-chloropyrimidine does not rearrange in the presence of methyl iodide at room temperature. At 100° molecular rearrangement takes place to give the completely rearranged compound, 1,3-dimethyl-4-chlorouracil.

2. 2,4,6-Trimethylpyrimidine rearranges in the presence of methyl iodide at room temperature, and more rapidly at higher temperatures, to give a mixture of the partially rearranged compound 2-oxy-3-methyl-4,6-

[12] Michael, *J. prakt. Chem.*, 49, 35 (1894).

dimethoxypyrimidine and the completely rearranged 1,3-dimethyl-4-methoxyuracil.

3. The preparation of 2-amino-4,6-dimethoxypyrimidine is described.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# 2-IODOFURAN AND 2-FURYLMAGNESIUM IODIDE

BY HENRY GILMAN, HARVEY E. MALLORY AND GEORGE F. WRIGHT

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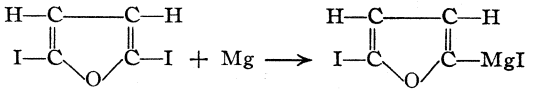
## Introduction

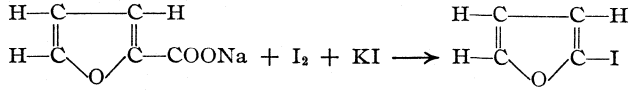
The chemistry of furan compounds is markedly circumscribed by present limitations on methods for the introduction of nuclear substituents, and by want of definite information on the positions assumed by substituents together with an inadequate understanding and formulation of rules of orientation. Within recent years, the number of direct nuclear substitution products of furfural and derivatives has been extended significantly. However, such substituents have not as yet lent themselves to widely diversified transformations.

One of several highly reactive key-groupings of this type, through which a miscellany of functions can be introduced indirectly, is the —MgX group attached to carbon. The ready reaction of 2,5-diiodofuran with activated




I

magnesium–copper alloy leading to the formation of 5-iodo-2-furylmagnesium iodide[1] suggested that the simple mono-iodofurans might react smoothly with magnesium to form the corresponding Grignard reagents. Unfortunately, however, no mono-iodofuran was known although attempts[2] have been made to prepare them. After a series of studies, we have devised a method for the preparation of pure 2-iodofuran from the accessible furoic acid and iodine.




II

Despite the fact that the present yield of 2-iodofuran is only 20% it is the most accessible simple halogen-furan which can be prepared conveniently in large quantities. 2-Iodofuran is not of a high order of stability, as might have been predicted from the known relative instabilities of chloro

[1] Gilman and Wright, *Iowa State Coll. J. Sci.*, **5**, 85 (1931).

[2] (a) Shepard, Winslow and Johnson, THIS JOURNAL, **52**, 2083 (1930); (b) Ciusa and Grillo, *Gazz. chim. ital.*, **57**, 323 (1927).

and bromofurans.[2a] However, it has so far offered no particular obstacles in manipulation, and it is, of course, more stable in dry ether solutions.

The reaction of 2-iodofuran leading to the formation of 2-furylmagnesium iodide proceeded with an ease that exceeded expectations, no activated magnesium–copper alloy being necessary. Of even greater importance is the excellent yield (95%) of Grignard reagent. Actually, this yield is in excess of that obtained with iodobenzene and is about equal to the yield of phenylmagnesium bromide.[3] This is not the first furylmagnesium halide, because 2-furylmagnesium bromide was prepared earlier[2a] from the less readily available 2-bromofuran by means of the activated magnesium–copper alloy. It is, however, the most accessible and unquestionably the most useful furan Grignard reagent despite the increasing number of such compounds prepared very recently, and in very high yields in some cases.[4] By means of 2-furylmagnesium iodide it should prove possible to prepare the widest variety of furan compounds with substituents in the 2-position. The immediately important applications are those turning on the proof of structure of some debatable mono-substituted furans and the synthesis of hitherto inaccessible types.

The general procedure for replacing carboxyl by iodine is one that can be extended from dehydromucic[1] and furoic acids to others like the alkyl and halogen substituted mono- and dibasic furancarboxy ic acids.[5] Another procedure which it is hoped will yield iodofurans is that involving the following sequence of reactions: nitro compound to amine to diazonium compound to iodo compound.[1]

## Experimental Part

**2-Iodofuran,** $C_4H_3OI$.—To a solution of 120 g. (3 moles) of sodium hydroxide in 2500 cc. of water is added 336 g. (3 moles) of furoic acid[6] and 332 g. (2 moles) of potassium iodide. This solution, contained in a 5-liter, round-bottomed flask provided with a reflux condenser, is heated in an oil-bath until the temperature of the mixture reaches 95–97°. Then 254 g. (1 mole) of iodine is added quickly[7] and the mixture refluxed for three hours by maintaining the oil-bath temperature between 130 and 140°.

At the end of the refluxing period, the flask and contents are cooled with tap water, and to the cooled mixture is added 200 to 500 cc. of a 10% solution of sodium thiosulfate to reduce any unaltered iodine. The solution is then steam distilled from a 12-liter flask until oil ceases to come over (about fifteen minutes). This oil is then subjected to another steam distillation, subsequent to a treatment with sodium thiosulfate to remove any iodine. The steam distillate is collected in two fractions. The first fraction

[3] Gilman, Zoellner and Dickey, THIS JOURNAL, **51,** 1576 (1929).

[4] Gilman and Hewlett, *Rec. trav. chim.*, in press. This article refers to other furan Grignard reagents.

[5] Among the studies for the preparation of 3-iodofuran is one starting with the known tetraiodofuran.

[6] The technical furoic acid used was purified by crystallizing once from water.

[7] It is necessary that the iodine be added rapidly. This can be effected by adding it at one time and promptly affixing the condenser to the reaction flask.

is collected in a short stemmed separatory funnel. The second fraction is collected as soon as the oil which steam distils becomes semi-solid in the condenser. The solid in the second fraction yields iodoform, to the extent of about 3.4 g. in a one mole run.

The first fraction is then distilled under reduced pressure, observing the following precautions. First, all parts of the distillation apparatus must be thoroughly steamed out or washed with dilute sodium hydroxide to remove traces of acid which induce resinification. Second, the capillary bubbling tube in the Claisen distilling flask is provided with a drying tube containing calcium chloride in order to dry incoming air. Third, the receiver is immersed in an iced-water bath. After carefully transferring the oil from the separatory funnel with a minimum of water, about 5 to 10 g. of anhydrous calcium chloride is added to the flask,[8] and the pressure is reduced immediately to about 15 mm. The 2-iodofuran distils at 43–45° (15 mm.) from a warm water-bath. At the first indication of decomposition in the water condenser, the pressure must be released[9] and the receiver removed immediately. The distillate weighs 39.5 g. (20% of the theoretical amount based on the iodine used); $d_{20}^{4}$ 2.024; $n_{D}^{20}$ 1.5661. The 2-iodofuran should be immediately diluted with anhydrous ether because it is relatively more stable in solution and because this ether solution can also be used for the preparation of the corresponding Grignard reagent.

*Anal.* Calcd. for $C_4H_3OI$: I, 65.46. Found: I, 65.26, 65.58.

**2-Furylmagnesium Iodide,** $C_4H_3OMgI$.—A solution of 35.4 g. (0.18 mole) of 2-iodofuran in 100 cc. of ether is added dropwise to a suspension of 6 g. (0.25 atom) of magnesium (either turnings or 30–80 mesh) in 50 cc. of ether contained in a 200 cc. three-necked flask provided with a mercury-sealed stirrer, condenser and dropping funnel. The reaction flask is previously swept out with dry, pure nitrogen. When the 2-iodofuran and the flask are dry, reaction sets in immediately without addition of iodine or other catalyst. The heat of reaction is large, and care must be exercised that not too much of the halide is added initially. When addition is complete, the mixture is refluxed for one-half hour and then preferably filtered in an inert atmosphere prior to use. Great care should be taken in opening the flask containing magnesium residues, after the Grignard solution is removed by filtration or decantation. The residues are unusually active and *ignite spontaneously* on contact with the air. They may be destroyed by the rapid addition of a large volume of water in an atmosphere of dry nitrogen. There is a possibility that the residues might contain some inflammable di-2-furylmagnesium. Analysis by the acid-titration method[3,10] showed that the Grignard reagent was formed in a 95% yield. Methyl red is recommended as an indicator for the titration of this RMgI compound because of the colored solution.

Two characteristic derivatives of the Grignard reagent were prepared. First, carbonation in a customary manner[11] gave furoic acid, $C_4H_3OCOOH$, in a 42.5% yield. Second, treatment with phenyl isocyanate gave furoyl anilide, $C_4H_3OCONHC_6H_5$, in an 85% yield. Each of these products was identified by mixed melting point determinations with authentic specimens. It was subsequently found by R. A. Franz that the

[8] The calcium chloride is present during the distillation, and the temperature of the water-bath is kept low enough to effect smooth distillation at the pressure indicated. A long stemmed funnel is recommended for the transferal in order to avoid having the iodide touch the side of the neck of the distilling flask.

[9] The pressure can be released by breaking the capillary bubbling tube against the side of the distilling flask. An inert atmosphere of dry nitrogen reduces decomposition during distillation.

[10] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45,** 150 (1923).

[11] Gilman and Parker, *ibid.*, **46,** 2816 (1924).

Grignard reagent can be prepared without distillation under reduced pressure, by separating carefully the steam-distilled iodide from water and subsequently drying its ether solution with barium oxide.

The authors are grateful to W. H. Zugschwerdt and E. A. Zoellner for experimental assistance, and to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for a grant which partially defrayed expenses.

## Summary

Pure 2-iodofuran has been prepared from furoic acid and iodine. It forms the corresponding Grignard reagent with uncommon ease and in excellent yields. Both compounds should prove suitable in determining the constitution of nuclear substituted furan compounds and in making accessible hitherto unavailable furan types.

AMES, IOWA

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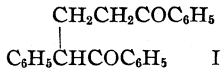
[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORY OF MCGILL UNIVERSITY]

# ADDITION REACTIONS OF VINYL PHENYL KETONE. II. DESOXYBENZOIN

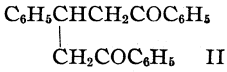
BY C. F. H. ALLEN AND W. E. BARKER[1]

RECEIVED SEPTEMBER 21, 1931 PUBLISHED FEBRUARY 5, 1932

In the first paper in this series[2] it was shown that β-chloropropiophenone could be used in place of vinyl phenyl ketone in addition reactions. In continuation of this work we have selected desoxybenzoin as addend, and compared the reactions of the 1,5-diketone (I) thus formed with those of the isomeric benzaldiacetophenone (II).[3]

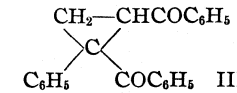


I

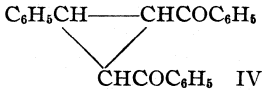


II

We have transformed it into cyclopropane derivatives (III) isomeric with those (IV) investigated by Kohler and Jones.[4]

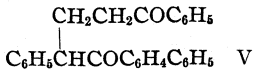


III

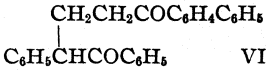


IV

We have also prepared two of the *p*-phenyl derivatives, one (V) by starting with *p*-phenyldesoxybenzoin and the other (VI) with *p*-phenyl-β-chloropropiophenone.



V



VI

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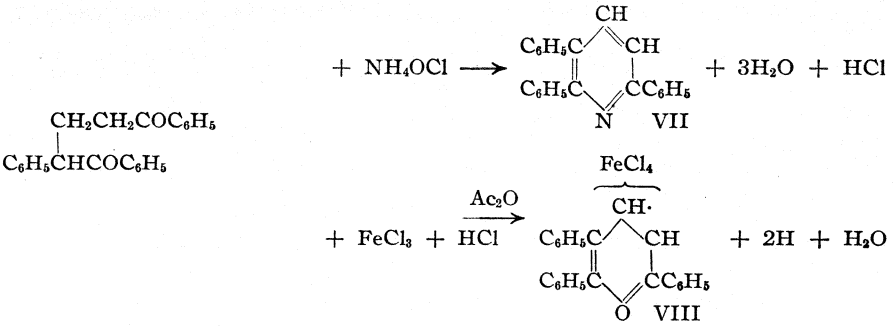
[1] Acknowledgment is hereby made of a bursary granted to one of us by the National Research Council of Canada.

[2] Allen and Bridgess, THIS JOURNAL, **51**, 2151 (1929).

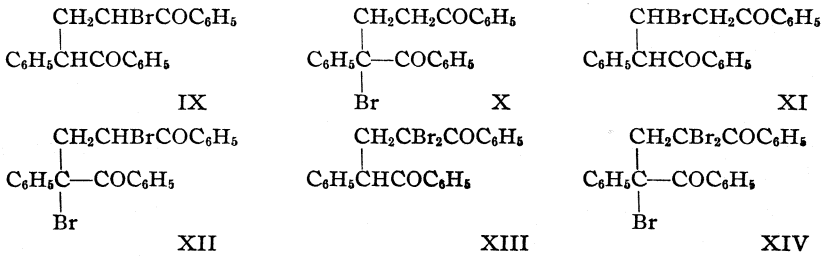
[3] Kostanecki, *Ber.*, **29**, 1493 (1891).

[4] Kohler and Jones, THIS JOURNAL, **41**, 1249 (1919).

$\alpha,\beta,\epsilon$-Triphenylpentanedione-$\alpha,\epsilon$ (I) formed a dioxime and also gave the two characteristic reactions of a 1,5-diketone, thus proving its structure; *e. g.*, it formed a pyridine derivative (VII) when heated in alcoholic solution with hydroxylamine hydrochloride, and an oxonium ferrichloride (VIII) by Dilthey's method.[5]



Since there are two carbonyl groups, each having alpha hydrogen, a considerable number of substitution products are possible as a result of bromination (structures IX to XIV).

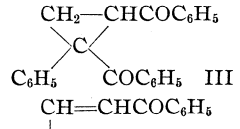


We have found two monobromides and two dibromides. Neither of the latter had any of the properties of keto-bromides, which would exclude the substances, represented by formulas XIII and XIV; accordingly they must be the stereoisomers XII.[6] The two monobromides are the stereoisomers as depicted in IX, since one can be changed into the other by the action of hydrogen bromide. We never isolated any monobromide corresponding to formula X. It may have been a major constituent of the gummy material left after the separation of the crystalline compounds, because on further bromination this residue always gave slightly more than half the calculated amount of the dibromides.

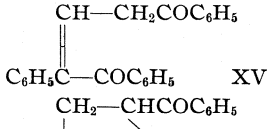
[5] Dilthey, *J. prakt. Chem.*, **94**, 65 (1916); **95**, 107 (1917); Dilthey and Quint, *ibid.*, **131**, 1 (1931).

[6] Any substance having bromine in the beta position (XI) would not only be unexpected, but definitely excluded because the same bromine compounds were also produced by the action of hydrogen bromide or bromine on the cyclopropane diketones, reactions which could not by any conceivable mechanism form $\beta$-bromo compounds.

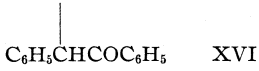
The cyclic diketones (III) were prepared by the usual methods developed by Kohler for closing a cyclopropane ring, elimination of hydrogen[7] bromide or bromine from the various bromine substitution products. This reaction might give one of three types of substances depending on the way in which the hydrogen bromide was eliminated; (A) a cyclopropane derivative (III) if the hydrogen and bromine came from the $\alpha$-$\gamma$ positions. (B) An ethylenic compound (XV, XVI) if they are removed from adjoining atoms. (C) A dihydrofuran derivative (XVII) if the elimination was from an enolic modification.



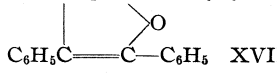
III



XV



XVI

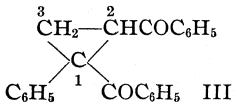


XVII

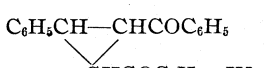
Both our substances formed dioximes, therefore neither was the furan derivative. They did not reduce permanganate, form an ozonide, nor decolorize bromine instantly; they added hydrogen bromide to regenerate the original monobromide, and very slowly reacted with bromine, forming the original dibromides. This evidence, taken all together, excludes the ethylenic isomers.

We were able to obtain both the possible stereoisomeric forms of phenyldibenzoylcyclopropane (III), the lower melting form being much more reactive. Although they are also 1,4-diketones, we did not notice any tendency toward the formation of furan derivatives. The lower melting form was changed into its less reactive isomer by allowing it to stand in an alcoholic solution containing potassium hydroxide. Both gave the same dioxime and monophenylhydrazone. Neither was affected by concd. sulfuric acid or by phosphorus pentachloride.

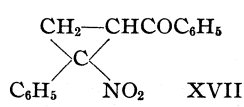
The more reactive, lower melting isomer exhibited properties like those of Kohler and Jones' isomeric cyclopropane diketone (IV), with this conspicuous difference, that when the ring was broken by any reagent,



III



IV

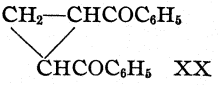


XVIII

*it was always opened in the 1,2-position.* This is in accord with the results from the nitrocyclopropane ketone (XVIII) which was also opened only in the 1,2-position,[1] and 1,2-dibenzoylcyclopropane (XX).[8]

[7] That the cyclopropane ring may be very easily closed in some instances is indicated by the fact that some of the cyclopropane can be isolated from the gummy residues from the preparation of the dibromide.

[8] Conant and Lutz, THIS JOURNAL, **49**, 1090 (1927); the ring was opened in the 1,2-position by reduction with zinc and acetic acid, which was the only reagent reported.



XX

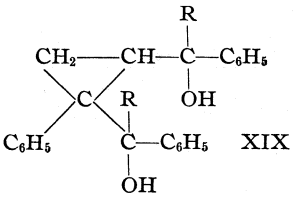
Kohler and his students have studied in great detail a large number of complex cyclopropane ketones containing unsaturated groups and have determined characteristic reactions of each type. In particular, it was often possible to open the ring at three different points, the most rigorous proof that any substance really contained such a ring. The mode of opening was determined by the substituent group present and the reagent used.

In the case of cyclopropane hydrocarbons, however, where reagents that rupture the ring are relatively few, the ring invariably opens between the carbon atoms that hold the largest and smallest number of substituent groups. With hydrogen bromide, the principal product is an alkyl halide in which the halogen is in combination with the carbon that holds the largest number of alkyl groups.[9]

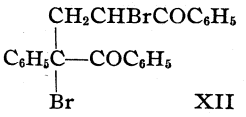
However, with the cyclopropanes that we have studied so far, that have substituent groups on only two of the carbon atoms, we find that when attacked the ring is always opened *between those carbons bearing the substituents*, regardless of the nature of the reagent. In view of the previous work, this is an unexpected result.

The lower melting cyclopropane derivative was slowly reduced by zinc and alcohol, rapidly by zinc and acetic acid, forming quantitatively the open chain diketone (I). Its isomer was unaffected by zinc in alcohol, but in acetic acid formed a sparingly soluble yellow substance with a high melting point and very large molecular weight. Because of its non-reactivity we were unable to determine its structure, but regard it as some sort of a polymeric reduction product. The same substance was also formed when a solution of the monobromide was boiled for a long time in *n*-butyl alcoholic solution.

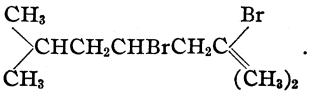
The lower melting, more reactive cyclopropane gave ditertiary glycols (XIX) with both phenylmagnesium bromide and methyl magnesium iodide.



XIX



XII

[9] Kishner [*J. Russ. Phys.-Chem. Soc.*, **45**, 957 (1913) from page 250 of Brooks, "The Non-Benzenoid Hydrocarbons," The Chemical Catalog Co., Inc., New York, 1922] reports that 1,1-dimethyl-2-isobutenylcyclopropane reacts in two steps with fuming hydrogen bromide to give  .

Its isomer gave only intractable gums with Grignard reagents. With hydrogen bromide the lower melting cyclopropane formed the more stable monobromide (IX). With bromine the principal product was the lower melting dibromide, but there was also present a small amount of its isomer. Since the latter dibromide was also formed during the bromination, it must have the structure as represented by XII, but we were unable to regenerate the cyclopropane from it. The higher melting isomer was not affected by hydrogen bromide, and only slightly by bromine; after prolonged action of the latter reagent a small amount of the higher melting open chain dibromide (XII) was formed.

We were unable to close the cyclopropane ring from the dibromide by elimination of hydrogen bromide, and thus secure a bromocyclopropane to compare with the one of Kohler and Jones; only intractable oils resulted from all efforts in that direction.

## Experimental

**Preparation of Starting Materials.**—Desoxybenzoin was prepared by the action of phenylacetyl chloride on benzene in the presence of anhydrous aluminum chloride; the details are described elsewhere.[10]

*p*-Phenyldesoxybenzoin was prepared by essentially the same procedure, using the same acid chloride and diphenyl[11] but with carbon disulfide as a solvent. After decomposing with ice and concd. hydrochloric acid the solvent and unused diphenyl were removed by steam distillation and the white product filtered and recrystallized by prolonged treatment with alcohol in a Soxhlet apparatus. The yield of ketone, melting at 151°, was 60%, based on the 68 g. of phenylacetic acid used. It has previously been prepared by Papcke.[12]

β-Chloropropiophenone was at first prepared by the directions of Hale and Britton[13] which are satisfactory for 10–20 g. lots. With larger quantities of reacting materials, a considerable amount of benzylacetophenone was produced; this was found to occur when a small amount of acid chloride in benzene solution was in contact with a relatively large amount of anhydrous aluminum chloride. This condition exists because the violence of the reaction, as described by these authors, requires drop by drop addition of the benzene–acid chloride mixture to the dry aluminum halide. By covering the latter with a large excess of benzene, the side reaction was made insignificant. We found no α-indanone, which might be expected according to recent patents.[14]

The directions were modified as follows: a mixture of 50 g. of β-chloropropionic acid and 45 g. of phosphorus trichloride was heated on a boiling water-bath for an hour, 200 cc. of dry benzene added and the solution decanted onto 75 g. of anhydrous aluminum chloride covered with 200 cc. of benzene, contained in a flask under a condenser; the reaction was mild and cooling of the flask unnecessary. The mixture was refluxed for

[10] "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. XII.

[11] We are indebted to the Dow Chemical Co., Midland, Michigan, for the diphenyl used in this work, and take this opportunity to express our appreciation of their assistance.

[12] Papcke, *Ber.*, **21**, 1339 (1888).

[13] Hale and Britton, THIS JOURNAL, **41**, 844 (1919).

[14] German Patent 485,309; Swiss Patent 126,404; *Chem. Abstracts*, **23**, 613 (1929).

an hour and worked up as previously described by Hale and Britton. The yields were 62–70 g. (80 to 90%) starting with 50 g. of β-chloropropionic acid.

The necessary β-chloropropionic acid was made by both published methods.[15] We found it much easier and simpler to make trimethylene chlorhydrin from the glycol and sulfur chloride;[16] although it had a disagreeable odor, this disappeared during the oxidation.

Benzylacetophenone was obtained in a 50% yield as follows: the β-chloropropionyl chloride prepared from 10 g. of the acid as previously directed was dissolved in 100 cc. of benzene and added to 30 g. of anhydrous aluminum chloride covered with 100 cc. of benzene; after refluxing one and a half hours it was decomposed by 200 g. of ice and 100 g. of concd. hydrochloric acid, the benzene extract separated, dried and solvent removed *in vacuo*. The residual brownish liquid solidified on cooling; it was washed with 25 cc. of low boiling petroleum ether and filtered; the residue weighed 8.5 g. and 1 g. more was obtained from the solution; yield, 9.5 g. (50%). It was identified by comparison with a sample on hand. This reaction is of interest because of Collet's work.[17]

*p*-Phenyl-β-chloropropiophenone, $ClCH_2CH_2COC_6H_4C_6H_5$-4, was made by allowing 50 g. of β-chloropropionic acid to react with 35 g. of phosphorus trichloride, taking up the acid chloride with 400 cc. of carbon disulfide, and adding it, drop by drop, with vigorous stirring to a mixture of 72 g. of diphenyl, 64 g. of anhydrous aluminum chloride and 400 cc. of carbon disulfide; a precipitate soon formed in a deep green liquid. After stirring for thirty minutes, the mixture was decomposed by 2000 g. of ice and 300 g. of concd. hydrochloric acid in a 5-liter flask, and the solvent and unused diphenyl steam distilled. The contents of the flask were cooled with stirring to prevent formation of a solid cake, and the product filtered and air-dried; yield 90–94 g. (80–84%). It was purified by recrystallizing from *n*-butyl ether (1 g. required 5 cc.). The use of alcohols had to be avoided since gelatinous precipitates resulted. *p*-Phenyl-β-chloropropiophenone forms fine rosets of needles that felt together and have a melting point of 112°. It is moderately soluble in the common organic solvents except ether and petroleum ether.

*Anal.* Calcd. for $C_{15}H_{13}OCl$: Cl, 14.5. Found: Cl, 14.2.

**Preparation of the Diketones.**—The 1,5-diketones were prepared by the reaction between the *p*-chloro ketone, desoxybenzoin, potassium acetate, and sodium methylate in methyl alcoholic solution, except with *p*-phenyldesoxybenzoin where *n*-butyl alcohol was used to secure better solubility. We were led to prepare the two phenylated diketones (V and VI) because of the difficulties encountered in handling the brominated product of the simple one; we hoped to secure less soluble derivatives with higher melting points, since it is well known that these properties are usually imparted by a phenyl group in the para position of simple substances.[18] Unfortunately in this instance they were found even more difficult to manipulate so were abandoned.

α,β,ε-Triphenylpentanedione-α,ε (I) was prepared as indicated by the equation

$$\begin{aligned} &ClCH_2CH_2COC_6H_5 \\ &+ C_6H_5CH_2COC_6H_5 \xrightarrow{NaOCH_3} \end{aligned} \quad \begin{matrix} CH_2CH_2COC_6H_5 \\ | \\ C_6H_5CHCOC_6H_5 \end{matrix} \quad \begin{aligned} &+ CH_3COOH + KCl \\ &+ CH_3COOK \end{aligned}$$

I

[15] "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. VIII, pp. 54, 58.

[16] Derick and Bissel, THIS JOURNAL, **38**, 2481 (1916).

[17] Collet [*Bull. soc. chim.*, [3] **17**, 66 (1897)] has studied the interaction of a number of halogenated acid chlorides and benzene, in the presence of anhydrous aluminum chloride and found that only the acyl halogen reacted.

[18] Drake and Bronitsky, THIS JOURNAL, **52**, 3715 (1930); Morgan and Pettet, *J. Chem. Soc.*, 1125 (1931).

To 4.5 g. of β-chloropropiophenone and 8 g. of potassium acetate in 50 cc. of warm methanol[19] were added 5 g. of desoxybenzoin and enough concentrated sodium methylate solution to give a definitely alkaline reaction to litmus. The reddish mixture was refluxed for an hour, acidified with acetic acid and filtered from precipitated salt, the latter being rinsed with 5 cc. of hot methanol. After three to four hours, buff colored crystals separated; these were dissolved in hot methanol (3 g. required 40 cc.), boiled with decolorizing carbon and filtered. Two recrystallizations then gave a pure white product, m. p. 95°; the average yield of a number of runs was 55%. This diketone forms large, white prisms, insoluble in petroleum ether, sparingly soluble in cold methanol, but very soluble in hot methanol and the other usual organic solvents.

*Anal.* Calcd. for $C_{23}H_{20}O_2$: C, 84.1; H, 6.1. Found: C, 84.0; H, 6.0.

**Derivatives.** (a) **Monoxime.**—The precipitated salt from a mixture of 1.4 g. of hydroxylamine hydrochloride, 4 g. of potassium acetate and 25 cc. hot alcohol was filtered and to the clear solution was added 3.3 g. of the diketone. After boiling for ten minutes and chilling the monoxime was deposited as white needles. After purification from alcohol it melted at 131°. It is insoluble in petroleum ether, sparingly soluble in ethyl ether and readily soluble in alcohol, chloroform and benzene.

*Anal.* Calcd. for $C_{23}H_{21}O_2N$: C, 80.4; H, 6.2. Found: C, 80.6; H, 6.0.

(b) **Dioxime.**—This was prepared in the same way, using twice the amounts of hydroxylamine hydrochloride and potassium acetate, and refluxing for three hours. It formed white needles from alcohol, m. p. 162°, with essentially the same solubilities as the monoxime.

*Anal.* Calcd. for $C_{23}H_{22}O_2N_2$: N, 7.8. Found: N, 8.0.

(c) **Mono-2,4-dinitrophenylhydrazone.**—This was prepared by the general method[20] and after crystallization from alcohol melted at 221°. It is moderately soluble in alcohol; readily soluble in ether, ethyl acetate and benzene.

*Anal.* Calcd. for $C_{29}H_{24}O_5N_4$: N, 10.8. Found: N, 11.0.

**2,3,6-Triphenylpyridine (VII).**—Two grams of the diketone and 0.9 g. of hydroxylamine hydrochloride in 25 cc. of methanol were refluxed for six hours, poured into water, and the precipitated gum crystallized from alcohol. It forms white needles, m. p. 115°, and is easily soluble in all the common solvents except petroleum ether.

*Anal.* Calcd. for $C_{23}H_{17}N$: C, 89.9; H, 5.5. Found: C, 89.9; H, 5.3.

This pyridine derivative gave only oils when attempts were made to form a methiodide and salt with methyl *p*-toluene sulfonate, but yielded a crystalline picrate. The latter was formed by heating to boiling 0.1 g. of the pyridine and 9.2 g. of picric acid in 5 cc. of alcohol and allowing to stand overnight. It separated from alcohol in yellow prisms, m. p. 163°; it is slightly soluble in ether and petroleum ether, readily soluble in alcohol, chloroform and benzene. For analysis, the picric acid was estimated by titration.

*Anal.* 0.0869 g. gave 0.0381 g. of picric acid; calcd. for $C_{29}H_{20}O_7N_4$: 0.0367 g.

**α-Phenyl-γ-(*p*-phenylbenzoyl)-butyrophenone** (V) was prepared by the same procedure. It forms white needles, m. p. 104°, insoluble in ether, but soluble in hot alcohol, chloroform and benzene.

*Anal.* Calcd. for $C_{29}H_{24}O_2$: C, 86.1; H, 5.9. Found: C, 86.0; H, 6.1.

[19] Unless otherwise specified, all the methanol used in this work was the synthetic 99% material obtained from the Commercial Solvents Corporation. By "alcohol" is meant 95% ethyl alcohol.

[20] Allen, THIS JOURNAL, **52**, 2955 (1930).

The dioxime was prepared as described above, and was purified, with difficulty, by dissolving in a small amount of ether and precipitating with petroleum ether. It formed a fine, white powder, m. p. 79–80°, and was readily soluble in all solvents except petroleum ether.

*Anal.* Calcd. for $C_{29}H_{26}O_2N_2$: N, 6.4. Found: N, 6.6.

**2,3-Diphenyl-6-xenylpyridine** was prepared in the same way as the triphenyl pyridine (VII). It separates from methanol, in which it is only moderately soluble, in fine, white needles, m. p. 193°; it is very soluble in benzene and chloroform.

*Anal.* Calcd. for $C_{29}H_{21}N$: N, 3.7. Found: N, 3.9.

**γ-Phenyl-γ-(*p*-phenylbenzoyl)-butyrophenone (VI)** was prepared similarly, using 5.6 g. of β-chloropropiophenone, 9.1 g. of *p*-phenyldesoxybenzoin, 10 g. of potassium acetate and 100 cc. of *n*-butyl alcohol. For purification, the butyl alcohol was removed by steam distillation, and the residual solid recrystallized from methanol; the yield was 60%. It forms white needles, m. p. 115°, that are moderately soluble in ether, petroleum ether and hot alcohol, and very soluble in benzene and chloroform.

*Anal.* Calcd. for $C_{29}H_{24}O_2$: C, 86.1; H, 5.9. Found: C, 85.8; H, 6.1.

The dioxime was made as previously described. It separated from methanol as a white powder, m. p. 214–215°; it is slightly soluble in hot alcohol, chloroform and benzene, but insoluble in ether and petroleum ether.

*Anal.* Calcd. for $C_{29}H_{26}O_2N_2$: N, 6.4. Found: N, 6.1.

**The Pyryllium Salts.**—These were prepared by a modification of Dilthey's method and isolated as ferrichlorides. The mechanism of the reaction is unknown but it was represented by Dilthey as shown in the introduction, although no free hydrogen ever appeared. His yields were of the order of 20%. It occurred to us that if some substance was added to remove this hydrogen as formed, the yields should be increased; we tried maleic anhydride and *p*-benzoquinone—the former was without effect, but the yields rose to 50% in the presence of one equivalent of the quinone.

One one-hundredth mole each of the diketone and quinone and 10 cc. of acetic anhydride were placed in a 100-cc. flask and 3 g. of technical ferric chloride was added; the mixture became very hot, turned dark and all the solid dissolved. When cold, the precipitated ferrichloride was filtered and washed with ether; it was analytically pure. Only intractable gums could be obtained from the filtrates, except with the *p*-phenyl substituted diketones, where small amounts were recovered unchanged. The properties are summarized in Table I.

TABLE I

SUMMARY OF PROPERTIES

| No. | -Butyrophenone | M. p., °C. | Formula | Fe analysis, % Calcd. | Found |
|---|---|---|---|---|---|
| 1 | γ-Phenyl-γ-benzoyl- (I) | Shr. 175, m. 189 | $C_{23}H_{17}OCl_4Fe$ | 11.0 | 10.8 |
| 2 | γ-Phenyl-γ-(*p*-phenylbenzoyl) (VI) | Shr. 180, m. 203 | $C_{29}H_{21}OCl_4Fe$ | 9.6 | 9.4 |
| 3 | α-Phenyl-γ-(*p*-phenylbenzoyl) (V) | 191–193 | $C_{29}H_{21}OCl_4Fe$ | 9.6 | 9.6 |

| No. | In water | $H_2SO_4$ addn. | Color |
|---|---|---|---|
| 1 | V. s. s., slight gr. fluores.; cloudy on standing or warming | Gr. yellow partial clearing | OY |
| 2 | Insol. | Yellow color, slightly gr. | OY |
| 3 | Insol. | Yellow color | Brick red |

**Bromination of the Diketones.**—All the diketones reacted readily with bromine, but the isolation of the products proved extremely difficult, and at times we despaired of ever securing any crystalline material. In contact with solvents and hydrobromic acid the crystalline substances rapidly became oily, and after removal of the solvent only highly colored, intractable gums were left. As previously stated, two isomeric monobromides (IX) and two dibromides (XII) were obtained.

(a) **Monobromination.**—In a 500-cc. flask fitted with stirrer, reflux condenser and dropping funnel were placed 16.4 g. of the diketone (I) and 25 g. of dry chloroform; the solution was warmed to 60° and 9 g. of bromine in 25 g. of chloroform added, drop by drop, with vigorous stirring; the greenish mixture boiled vigorously as hydrogen bromide was copiously evolved. Stirring was continued for five minutes after all the bromine had been added and the solution then poured into 300 cc. of cold alcohol. The white, solid monobromide slowly separated and was filtered after four hours; the filtrate usually deposited a little more of the same solid, but on complete evaporation left only a brownish gum, which was further brominated as described below. The monobromide was purified by repeated crystallization from ethyl acetate or benzene (alcohols must be avoided). The yield of purified material was 11–13 g., 50–55%, m. p. 152°. It forms fine plates almost insoluble in alcohol, but readily soluble in hot ethyl acetate, benzene and chloroform.

The stereoisomer was not found during any preparation of the monobromide, but only by fractional crystallization of the solid resulting from dibromination. It melts at 150° (by the dip method) and a mixed melting point with the 152° form melts at 135°.

*Anal.* Calcd. for $C_{23}H_{19}O_2Br$: Br, 19.6. Found: (150°) Br, 19.7; (152°) Br, 19.9.

When a solution of the 150° isomer in glacial acetic acid was saturated with hydrogen bromide it was quantitatively changed into its stereoisomer.

(b) **Dibromination.**—To 32 g. of the diketone in 20 g. of dry chloroform, using the above apparatus, was added, drop by drop, 32 g. of bromine in 10 g. of the same solvent; bromination started readily after heating the flask in one spot with a match, but it was necessary to keep the temperature below 40° to get the best yields. When all the bromine had been added, 150 cc. of methanol was introduced and the flask cooled in running water for five minutes; a mixture of gum and fine needles separated and was filtered. This was dissolved in 500 cc. of boiling alcohol, filtered from 0.5 g. of insoluble residue and cooled with stirring. Final purification from methanol gave white needles, m. p. 127°. The yield was 11–13 g., or 39–40%. It is slightly soluble in ether and petroleum ether, moderately soluble in hot alcohol, but readily dissolves in benzene and chloroform.

The original filtrate, after standing overnight, deposited 7 g. (14–15%) of short thick needles of the 150° monobromide. None of this was found if the temperature of the bromination mixture rose above 40°.

On further bromination in boiling chloroform solution both monobromides yielded the 127° dibromide; a dried chloroform solution of the residual gums from monobrominations also gave small amounts of this same dibromide on further treatment with bromine.

The insoluble residue above, on fractional crystallization from ethyl acetate, was separated into 150° monobromide and a second dibromide; the latter was also formed by the action of bromine on the cyclopropane derivatives (see below). It formed diamond-shaped plates from ethyl acetate, m. p. 180°, which are sparingly soluble in hot alcohol, moderately soluble in ether and hot ethyl acetate, and very soluble in benzene and chloroform.

*Anal.* Calcd. for $C_{23}H_{18}O_2Br_2$: Br, 32.9. Found: (127°) Br, 32.8; (180°) Br, 32.5.

Neither dibromide could be changed into the other, but they must have structure (XII), since both are obtained by bromination of the diketone and the cyclic compounds.

**The Cyclopropane Diketones (III).**—Both the possible stereoisomeric cyclopropane derivatives were obtained from the two monobromides and one dibromide, and small amounts could be isolated from the residual gums from the brominations. The lower melting form was quantitatively changed into its isomer by alcoholic potash. Both forms yielded the same dioxime and monophenylhydrazone.

(a) **From the Dibromide.**—In a 500-cc. flask fitted with a stirrer and reflux condenser were placed 10 g. of the 127° dibromide, 10 g. of potassium iodide, 200 g. of mercury, 200 cc. of methanol, and 60 cc. of water; the whole was set on a boiling water-bath and stirred vigorously to expose as large a mercury surface as possible; the dibromide slowly dissolved and a clear yellow solution resulted after an hour. It was decanted from the mercury and filtered hot; after cooling at the tap a solid, contaminated with a little gum, separated. On recrystallization from methanol, 5 g. (75% yield) of cyclopropane was obtained. It forms white needles, m. p. 123°, which are insoluble in petroleum ether but soluble in the other solvents. The 180° dibromide was recovered unchanged after a similar treatment; the use of zinc and alcohol left an oil.

The isomeric cyclopropane diketone was prepared from this one by allowing a solution in 1% alcoholic potash to stand overnight. It forms white needles that melt at 126°, and are somewhat less soluble than the isomer in the same solvents; it is often slightly yellowish and the color is very difficult to remove.

*Anal.* Calcd. for $C_{23}H_{18}O_2$: C, 84.7; H, 5.5. Found: (123°) C, 84.6; H, 5.7; (126°) C, 84.9; H, 5.2.

The 126° isomer was obtained in considerable quantity by refluxing alcoholic solutions of the gummy residues accumulated during the dibrominations for five to eight hours, and allowing to stand for one to five days. Gummy, yellow crystals separated, and were dissolved in ether and filtered from traces of a yellow, insoluble substance; treated in this way, 40–45 g. of gum would yield 20–25 g. of cyclopropane. As the constituents of the gum are uncertain the mechanism of the reaction is unknown; it would certainly be remarkable that bromine or hydrogen bromide should be lost so easily from any of the possible bromo ketones.

In attempts to obtain a bromocyclopropane the dibromides were treated with one equivalent of potassium acetate; the higher melting substance was recovered unchanged, while its isomer gave an intractable gum.

(b) **From the Monobromides.**—The lower melting monobromide reacted with alkaline reagents to form the cyclopropane; an 8–10% alcoholic potash solution gave a 74% yield of the 126° isomer. Potassium acetate in glacial acetic acid gave a mixture of both forms, largely the higher melting isomer, in a yield of 30%. Heated for five to seven hours with potassium iodide and mercury the yield varied from 40 to 45%, but was almost entirely the lower melting form; the reaction took place without the mercury in which case it was very difficult to get a colorless product.

In marked contrast, the higher melting monobromide gave only traces of crystalline material with a great variety of alkaline reagents; from the gums thus produced, a 1–2% yield of the monophenylhydrazone of the cyclopropane diketone could be isolated, but on dissolving the gums in acetic acid and saturating with hydrogen bromide a 50–60% recovery of the same monobromide could be realized.

**Dioxime.**—Although both cyclopropane derivatives yielded the same dioxime when treated with hydroxylamine hydrochloride and potassium acetate in the usual manner, neither isomer was changed into the other by potassium acetate alone. A mixture of 0.5 g. of hydroxylamine hydrochloride, 1 g. of potassium acetate and 1 g. of the diketone in 20 cc. of alcohol was refluxed for twenty-four hours. It deposited

20% of the calculated amount of white needles, that were purified by recrystallizing from 50% alcohol. The dioxime melts at 212°, is moderately soluble in alcohol and readily soluble in the other solvents except petroleum ether.

*Anal.* Calcd. for $C_{23}H_{20}O_2N_2$: C, 77.5; H, 5.6. Found: C, 77.6; H, 5.7.

**Monophenylhydrazone.**—Both isomers gave the same monophenylhydrazone. Yields of the order of 2% were also obtained from the gums that resulted in all attempts to prepare the cyclopropanes from the 152° monobromide. One gram each of phenylhydrazine hydrochloride and potassium acetate was dissolved in 25 cc. of hot alcohol and filtered (pure phenylhydrazine base gave no better result), 0.5 g. of cyclic diketone added, the whole refluxed for five minutes and allowed to evaporate spontaneously. After several days, a reddish gum containing the desired substances was left; the gum was removed by washing with ether and the solid recrystallized from alcohol. The monophenylhydrazone forms fine, white needles, m. p. 169°, insoluble in ether and petroleum ether, but soluble in alcohol and chloroform.

*Anal.* Calcd. for $C_{29}H_{24}ON_2$: N, 6.7. Found: N, 7.0.

**Reactions of the Cyclopropane Diketones.**—As previously stated the only effect of alkaline reagents was to change the lower melting form into its isomer. Neither was affected by permanganate or concd. sulfuric acid, and was almost quantitatively recovered after treatment with phosphorus pentachloride in benzene solution. Neither could be reduced catalytically using Adams' catalyst. All the other reagents tried gave different results with the isomers; the lower melting form always showed the greater activity.

With zinc dust and alcohol or acetic acid, the active isomer was reduced to the open-chain diketone (I); the reaction was rapid and complete in acetic acid, but in alcohol a mixture resulted. Under the same conditions the diketone (I) was not affected.

A mixture of 0.5 g. of the 123° cyclopropane derivative, 2 g. of zinc dust, 30 cc. of alcohol and 5 cc. of water was refluxed for an hour, filtered hot, and allowed to evaporate spontaneously; it left a mixture, two-thirds rosets and the rest plates; the latter was the diketone and the former the starting material, both identified by mixed melting points. When 15 cc. of glacial acetic acid and 1 cc. of water was substituted in the above the yield of open-chain diketone was quantitative.

The less active cyclic compound was unchanged after prolonged boiling with zinc dust and alcohol, even at the boiling point of tetralin containing capryl alcohol. In acetic acid the solution quickly turned bright yellow, and a yellow solid separated; after an hour this, in suspension, was easily decanted from the heavier zinc; 0.4 g. was obtained from 0.5 g. of starting material. It is soluble in boiling xylene and aniline, very sparingly soluble in benzene, and insoluble in the other usual organic solvents, including dioxane and camphor; it melts at 282°. It did not react with bromine nor permanganate (there was a slight action on long standing), nor phenyl isocyanate, evolved methane but was recovered unchanged on treatment with methylmagnesium iodide, gave a magenta color with concd. sulfuric acid, and an oil with phosphorus pentachloride. In boiling aniline it gave values for molecular weight of the order of 3000; in the Grignard machine[21] it showed one active hydrogen for every unit of 320–330. We did not analyze it. It was also formed in small quantities from the 152° monobromide, 127° dibromide, and gummy residues from all brominations by prolonged boiling in butyl alcoholic solution. It is, doubtless, some sort of a reduction product, possibly a condensation polymer.

The higher melting cyclopropane derivative is not affected by hydrogen bromide; its isomer reacted readily, regenerating the known monobromide, m. p. 152°—the ring was opened where it had been closed, in the 1,2-position.

[21] Kohler and Richtmyer, THIS JOURNAL, **52**, 3736 (1930).

A solution of 0.5 g. of the 123° isomer in 20 cc. of glacial acetic acid was saturated with hydrogen bromide; it became warm and slightly colored. The next day a quantitative yield of the 152° dibromide had separated, and was identified by mixed melting point.

With bromine the 123° cyclopropane diketone gave mainly the 127° dibromide but there was always a small amount of its isomer, m. p. 180°. However, the higher melting cyclic compound was mainly recovered unchanged, but after prolonged treatment always gave a small amount of the 180° dibromide; the ring was again opened in the 1,2-position.

To a solution of 5 g. of the 123° cyclopropane derivative in 10 g. of chloroform was added 2.5 g. of bromine, and the mixture warmed; a trace of hydrogen bromide was noticed. After fifteen minutes, 50 cc. of methanol was added and the solution cooled in ice water for two hours; 3.2 g. of the dibromide separated—a very small amount was obtained from the filtrate, making a total yield of 43%. It was carefully fractionally crystallized into two components, mostly the 127° isomer, but always with 50–60 mg. of the 180° form. By a similar procedure, over 90% of the 126° cyclopropane was recovered unchanged; from 5 g. of starting material 20 mg. of the 180° dibromide was secured.

The two cyclopropane diketones gave different results with organic magnesium compounds. The lower melting form gave ditertiary alcohols as expected; its isomer reacted but gave only a trace of solid, the rest being a gum.

In the usual Grignard apparatus, phenylmagnesium bromide was prepared from 2 g. of magnesium, 12 g. of bromobenzene and 50 cc. of ether; the reagent was well cooled and 5 g. of the solid cyclic diketone (123°) added in small amounts. After refluxing for an hour and working up in the usual way, a 40% yield of 1-phenyl-1,2-(diphenylcarbinyl)-cyclopropane (XIX, R = $C_6H_5$) was obtained. It formed diamond-shaped plates, m. p. 168°, insoluble in cold alcohol, but readily soluble in hot alcohol, ether, benzene and chloroform.

*Anal.* Calcd. for $C_{35}H_{30}O_2$: C, 87.1; H, 6.2; mol. wt., 482. Found: C, 87.3; H, 5.8; mol. wt., 477.

On treatment with an excess of methylmagnesium iodide, methane was evolved, and after decomposing the complex with acid the glycol was recovered.

In the same way 1-phenyl-1,2-(phenylmethylcarbinyl)-cyclopropane was prepared from the 123° cyclopropane and methylmagnesium iodide; after acidification the product, which was insoluble in ether, was filtered; the yield was 45%. This glycol forms short, thick rods, m. p. 196°, insoluble in ether, moderately soluble in hot alcohol and hot ethyl acetate and readily soluble in benzene and chloroform.

*Anal.* Calcd. for $C_{25}H_{26}O_2$: C, 83.8; H, 7.3. Found: C, 83.6; H, 7.2.

It also was recovered unchanged when treated with an excess of methylmagnesium iodide; in the Grignard machine it consumed two moles of reagent and evolved two moles of gas.

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## Summary

1. Desoxybenzoin adds to vinyl phenyl ketone to form a 1,5-diketone.

2. The diketone has been transformed into bromine substitution products, a pyridine derivative and an oxonium salt.

3. Two cyclopropane diketones were prepared from the various

bromo diketones; one is much more reactive than the other, and has been compared with a previously known structural isomer.

4. In all reactions in which the cyclopropane ring is attacked it is opened in the position in which it was closed, the 1,2-position, regardless of the nature of the reagent. This regularity is in marked contrast to the results found by previous investigators in cyclopropane chemistry.

MONTREAL, CANADA

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF VICTOR CHEMICAL WORKS]

# SULFUR ADDITION WITH THE AID OF THIOPHOSPHORYL CHLORIDE AND THE CATALYSIS OF TRIARYL THIOPHOSPHATE FORMATION

BY H. BILLROTH GOTTLIEB

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Up to the present, thiophosphoryl chloride has not been used as a source of sulfur for the addition of sulfur to organic compounds. Some observations of this type of reaction of thiophosphoryl chloride were made and are described below.

Thiophosphoryl chloride changed triphenyl phosphite into triphenyl thiophosphate, tri-*o*-cresyl phosphite into tri-*o*-cresyl thiophosphate and diphenylmonochlorophosphite into diphenylmonochloro thiophosphate. The method of preparation consisted in mixing equimolecular amounts of organic phosphite and thiophosphoryl chloride, warming the mixture until reaction occurred, which was very violent at the start. It was completed by refluxing and the products were isolated by fractional distillation.

Phosphorus trichloride distilled over first. Then the thiophosphate formed was distilled *in vacuo*. This transfer of sulfur from the thiophosphoryl chloride to the organic phosphite proceeds without side oxidations. The thiophosphate is colorless. Sulfur additions to organic phosphites have been carried out previously by heating organic phosphites with flowers of sulfur.[1] However, in this latter method yellowish-colored side products are formed, which are not readily separated from the thiophosphate.

The addition of sulfur with the aid of thiophosphoryl chloride, as described above, affords an explanation for an interesting catalysis in thiophosphate formation. If pure thiophosphoryl chloride, rectified by distillation, is refluxed with a phenol, only little triaryl thiophosphate may be obtained. The addition of small amounts of phosphorus trichloride catalyzes the reaction in a high degree. When 3 moles of phenol are refluxed with 1 mole of very pure thiophosphoryl chloride, one obtains after seven

[1] (a) Anschütz and Emery, *Ann.*, **253**, 117, 118 (1889); (b) Walter Broeker, *J. prakt. Chem.*, [2] **118**, 287–294 (1928).

hours only a 16% yield of triphenyl thiophosphate. If on the other hand the experiment is carried out under the same conditions with the sole exception that 1.8% (by weight) of phosphorus trichloride is added to the thiophosphoryl chloride, the yield of triphenyi thiophosphate is 99.5%. The very plausible explanation of this catalysis is that triphenyl phosphite is formed first from the phenol and the small amounts of phosphorus trichloride present and that to this phosphite the thiophosphoryl chloride gives off its sulfur, regenerating phosphorus trichloride.[2]

In the sulfur additions with thiophosphoryl chloride the phosphorus–sulfur linkage is broken and the sulfur migrates. The alternative explanation would be the assumption of migrating phenoxy groups. To disprove the latter explanation, it was shown that phosphenyl chloride and thiophosphoryl chloride react with each other when refluxed, yielding phosphorus trichloride and phosphenpl thiochloride. This compound has been formed previously by the addition of elementary sulfur to phosphenyl chloride,[3] and by the reaction of sulfur monochloride with phosphenyl chloride.[4] In this case sulfur migration is the only assumption which may explain the outcome of the experiment, since the carbon–phosphorus linkage is certainly kept unchanged under the mild conditions of refluxing the two liquids. H. Köhler[4] has already remarked that the sulfur has a greater affinity for the phosphorus in phosphenyl chloride than for the phosphorus in phosphorus trichloride, since sulfur monochloride reacts violently with the former, but does not react with the latter, unless heated under pressure. Of this greater affinity the reaction of thiophosphoryl chloride with phosphenyl chloride is further evidence.

## Experimental Part

**Triphenyl Phosphite.**—This compound was obtained in particularly pure form and crystallized. No melting point has been reported in the literature, the triphenyl phosphite being described as a liquid. One mole of phosphorus trichloride and three moles of phenol reacted in an all-glass reflux apparatus. The temperature during the reaction did not exceed 205°. The product was rectified twice in a Claisen flask with a very high neck to avoid any contact of the high boiling liquid with stoppers. The product boiled at 209–210° at 1 mm. and crystallized readily when cooled in an ice–salt mixture. The melting point was +17° to 22°.

*Anal.* Calcd. for $(C_6H_5O)_3P$: P, 10.1. Found: P, 10.2.

**Triphenyl Thiophosphate.**—One gram mole of triphenyl phosphite was mixed with one gram mole of thiophosphoryl chloride at room temperature in a flask connected with a coil condenser. The mixture was cautiously heated to 55°. A violent reaction

[2] It should be mentioned that other substances like sulfomonochloride, amines and in particular thionyl chloride and ferrous chloride have been found to exert some catalytic action in the formation of triaryl thiophosphates from phenols and thiophosphoryl chloride.

[3] H. Köhler and A. Michaelis, *Ber.*, **9**, 1053 (1876).

[4] H. Köhler, *ibid.*, **13**, 463 (1880).

ensued, during which phosphorus trichloride was liberated and caught in a receiver joined to the coil condenser; 116 g. of phosphorus trichloride was obtained. The temperature was raised to 160° to complete the reaction and to expel the phosphorus trichloride. Then the mass was subjected to fractional distillation *in vacuo*. The fraction distilling at 230–240° at 1 mm. (the bulk came over at 232°) solidified at 48° and was practically pure triphenyl thiophosphate, 225 g. (65% yield).

**Tri-*o*-Cresyl Thiophosphate.**—35.2 Grams of rectified tri-*o*-cresyl phosphite was mixed with 16.3 g. of thiophosphoryl chloride. The experiment was carried out as in the preceding case of the phenol derivative; 11 g. of phosphorus trichloride was caught and determined as such. The fraction distilling at 260–265° at 1 mm. solidified after eighteen hours' standing at 0°. Its melting point was 45°. It was pure tri-*o*-cresyl thiophosphate. The preparation was mixed with tri-*o*-cresyl thiophosphate prepared from thiophosphoryl chloride and *o*-cresol. The melting point of the mixture was 44.8°.

**Diphenylmonochloro Thiophosphate.**—Thirty grams of diphenyl monochlorophosphite $(C_6H_5O)_2PCl$ (b. p. 165–174° at 1 mm.) was mixed with 16 g. of thiophosphoryl chloride and refluxed for one hour. In the subsequent fractional distillation, 10 g. of phosphorus trichloride was obtained. At 180–183° at 1 mm., 22 g. of diphenylmonochloro thiophosphate came over. It melted at 64°.

**Phosphenyl Thiochloride ($C_6H_5PSCl_2$).**—Equimolecular amounts of thiophosphoryl chloride and rectified phosphenyl chloride (twice distilled *in vacuo* to purify from phosphorus) were heated to 115°. At this temperature reaction set in. It was completed by boiling gently for three hours. The product was then subjected to fractional distillation. Phosphorus trichloride came over first. The remaining compound was subjected to vacuum distillation. At 150° (26 mm.) a colorless oil came over, which had an aromatic odor. The heavy oil was fairly stable to water and had all the properties of phosphenyl thiochloride.

*Anal.* Calcd. for $C_6H_5PSCl_2$: S, 15.1; P, 14.7. Found: S, 15.0; P, 14.4.

**The Catalytic Effect of Phosphorus Trichloride on the Formation of Thiophosphates.**—141 Grams of phenol and 84.5 g. of thiophosphoryl chloride were refluxed in an all-glass apparatus. The thiophosphoryl chloride employed was pure, having been rectified through a column; it boiled at 122.6–124.2° (740.6 mm.). The liberated hydrochloric acid gas was titrated. After three hours only 7.8% of the theoretical amount of hydrochloric acid to be expected in triphenyl thiophosphate formation had come over, after thirty hours, only 35% hydrochloric acid. In another experiment carried out under precisely the same conditions, 1 cc. of phosphorus trichloride (0.68% of total reaction mass or 1.8% of the weight of thiophosphoryl chloride employed) was added. After three hours 41% of the hydrochloric acid had come over and after seven hours of refluxing, 99.5%. The reaction was complete.

## Summary

Some organic phosphorus derivatives containing trivalent phosphorus are capable of being oxidized by thiophosphoryl chloride.

Small amounts of phosphorus trichloride catalyze the formation of triaryl thiophosphates from phenols and thiophosphoryl chloride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# NUCLEAR SYNTHESES IN THE OLEFIN SERIES. III.[1] THE HEXENES

BY CLAUDE G. SCHMITT[2] AND CECIL E. BOORD

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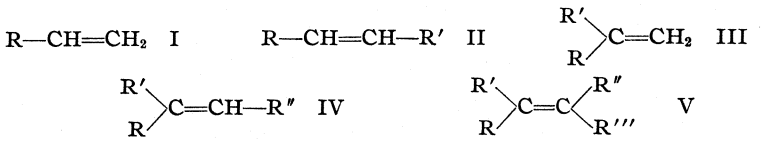
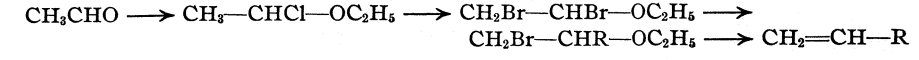
The nuclear synthesis of olefins through the β-bromo ethers has proved of general application and it is now possible to undertake a systematic survey of the hexenes. Ten of the thirteen possible structurally isomeric hexenes, including all the unknown members of the family, have been prepared by this method. The preparation of the remaining three involves such difficulties of technique it seems advisable to publish the data in hand at the present time.

The physical constants of the thirteen possible hexenes have been assembled in Table I. The values taken from the literature are those which seem most reliable. A mere cursory examination of the table reveals striking relationships between the physical constants of the olefins and the position of the double bond within the molecular structure.

The simple olefins may be divided into five types depending upon the number and position of the alkyl groups attached to the ethylene group.



The first paper of this series[1b] described the application of the β-bromo ether synthesis to α-olefins, type I.



In the present paper the same principle has been applied in the preparation of 1-hexene, 4-methyl-1-pentene and 3-methyl-1-pentene. The preparation of *tert.*-butylethylene (3,3-dimethyl-1-butene) by this method has not been successful for reasons not fully understood. This is one of the three hexenes upon which further work must be done before it can be stated definitely whether the method will apply.

The second paper in the series[1c] described the application of the synthesis

[1] For the previous papers in this series see: (a) Swallen and Boord, THIS JOURNAL, **52**, 651 (1930); (b) Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930); (c) Shoemaker and Boord, *ibid.*, **53**, 1505 (1931); (d) see also Schmitt and Boord, *ibid.*, **53**, 2427 (1931).

[2] This paper is abstracted from the dissertation presented by Claude Gordon Schmitt in partial fulfilment of the requirements for the degree of Doctor of Philosophy, to the Faculty of the Graduate School of The Ohio State University, June, 1931.

Presented in part on the program of the Organic Division at the Indianapolis meeting of the American Chemical Society, April, 1931.

to the 1,4-diolefins. 1,4-Hexadiene and 1,4-heptadiene were derived by using propionaldehyde and *n*-butyraldehyde, respectively, in the place of acetaldehyde in the initial step of the synthesis. This work showed that the method could be used in preparing $\beta$- and $\gamma$-olefins.

$$R{-}CH_2{-}CHO \longrightarrow R{-}CH_2{-}CHCl{-}OC_2H_5 \longrightarrow R{-}CHBr{-}CHBr{-}OC_2H_5 \longrightarrow$$
$$R{-}CHBr{-}CHR'{-}OC_2H_5 \longrightarrow R{-}CH{=}CH{-}R'$$

In the present investigation the same principle has been applied to the preparation of 2-hexene, 3-hexene and 4-methyl-2-pentene, all symmetrical dialkyl derivatives of ethylene, type II.

In a recent number of THIS JOURNAL, Lauer and Spielman[3] have shown that $\beta$-bromo ethers when heated with finely powdered, anhydrous potassium hydroxide yield $\alpha,\beta$-unsaturated ethers. This reaction opens an avenue whereby the $\beta$-bromo ether synthesis of olefins can be readily extended to include the unsymmetrical dialkyl derivatives of ethylene, type III. The additional steps involved are apparent from the following scheme

$$CH_2Br{-}CHR{-}OC_2H_5 + KOH \longrightarrow CH_2{=}CR{-}OC_2H_5 + KBr + H_2O$$
$$CH_2{=}CR{-}OC_2H_5 + Br_2 \longrightarrow CH_2Br{-}CBrR{-}OC_2H_5$$
$$CH_2Br{-}CBrR{-}OC_2H_5 + R'{-}MgBr \longrightarrow CH_2Br{-}CR(R')OC_2H_5 + MgBr_2$$
$$CH_2Br{-}CR(R')OC_2H_5 + Zn(Alc.) \longrightarrow CH_2{=}CR(R') + C_2H_5OZnBr$$

This modification of the synthesis has been used to prepare 2-methyl-1-pentene, 2,3-dimethyl-1-butene and 2-ethyl-1-butene.[1d]

Whether the method can be extended through the $\alpha,\beta$-unsaturated ethers derived from the $\beta$-bromo ethers corresponding to the higher aldehydes is now under investigation. Should this work prove successful it may be possible to apply the nuclear synthesis to the trialkyl derivatives of ethylene, type IV, and the tetra-alkyl derivatives of ethylene, type V. 2-Methyl-2-pentene was prepared from isobutyraldehyde as a special case under type II. 3-Methyl-2-pentene and 2,3-dimethyl-1-butene have not yet been prepared by this method.

When one examines the literature of the hexenes he finds much confusion. The first hydrocarbon of this family was obtained by the destructive distillation of bog-head coal.[4] The earliest synthetic product was prepared by the action of alkalies upon the hexyl iodide from mannite.[5]

Both of these products boiled with temperature range 68–70° and early investigators were inclined to review them as $\alpha$-hexene.[6] This view was definitely proved to be in error by Otto Hecht,[7] who oxidized the hexene from mannite with the formation of acetic and *n*-butyric acids, showing it to be a $\beta$-olefin.

[3] Lauer and Spielman, THIS JOURNAL, **53**, 1533 (1931).
[4] Williams, *Ann.*, **108**, 384 (1858).
[5] Erlenmeyer and Wanklyn, *ibid.*, **135**, 141 (1865).
[6] Schorlemmer, *ibid.*, **177**, 313 (1875); Brochet, *Bull. soc. chim.*, [3] **7**, 568 (1892).
[7] Hecht, *Ber.*, **11**, 1152 (1878).

In general those methods involving pyrolysis such as the dehydration of an alcohol or the decomposition of a quaternary ammonium salt are likely to cause a migration of the double bond. In such a case the olefin obtained may not have the structure indicated by the synthesis. Boiling an unsaturated compound with alcoholic potash is also a well-known method for shifting the position of a double bond.[8] This fact leads one to accept, with some reservation, the structure of those olefins prepared by many of the methods commonly used.

A second source of confusion in the literature of the hexenes arises from the fact that several of them were first prepared by the dehydration of pinacolin alcohol. During the early work the structure of pinacolin alcohol itself was in doubt[9] and later it was shown to be a mixture or at least to yield a mixture of bromides,[10] giving rise to a number of hexenes.

These considerations lead one to place the greatest reliance on those methods requiring only low temperatures such as the action of alkylmagnesium halides upon allyl bromide[11] or of metallic zinc upon the corresponding dibromide in alcoholic solution.[12]

The present method has an added advantage in that the nucleus is built up by definitely known steps, the double bond being introduced in the final step at a temperature which need not exceed the boiling point of propyl alcohol.

## Physical Properties and Structure

In previous communications we formulated certain tentative rules relating the boiling point of an olefin to its structure. It will be observed from Table I that 1-hexene boils lower than 2-hexene and 4-methyl-1-pentene lower than 4-methyl-2-pentene. Indeed 4-methyl-1-pentene boils lower than either of the two forms of 4-methyl-2-pentene. These facts support the previous conclusion that *α-olefins boil lower than β-olefins.*

A further inspection of Table I shows an interesting sequence in the physical constants of the hexenes of type I. *Tert.*-butylethylene (3,3-dimethyl-1-hexene) boils lower than either *sec.*-butylethylene (3-methyl-1-pentene) or isobutylethylene (4-methyl-1-pentene) and these in turn lower than *n*-butylethylene (1-hexene). Among the hexenes of type II, both forms of 4-methyl-2-pentene boil lower than 2-hexene and among

[8] Eykman, *Ber.*, **23**, 855 (1890); Ciamician and Silber, *ibid.*, **23**, 1159, 1164 (1890); Thiele and Henle, *Ann.*, **347**, 310 (1906).

[9] Couturier, *Ann. chim. phys.*, [6] **26**, 460 (1892).

[10] Delacre, *Bull. soc. chim.*, [3] **35**, 811 (1906); Zelinsky and Telikow, *Ber.*, **34**, 3249 (1901).

[11] (a) Brooks and Humphrey, THIS JOURNAL, **40**, 829 (1918); (b) Kirrmann, *Bull. soc. chim.*, [4] **39**, 990 (1926); (c) Mlle. v. Risseghem, *Bull. soc. chim. Belg.*, **35**, 345 (1926).

[12] (a) Gladstone and Tribe, *Ber.*, **7**, 364 (1874); *J. Chem. Soc.*, **21**, 306 (1878); (b) Lespieau and Wiemann, *Bull. soc. chim.*, **45**, 627 (1929).

TABLE I

THE PHYSICAL CONSTANTS AND CONSTITUTION OF THE HEXENES

| Structure | Type | B. p., °C. (760 mm.) | $d_4^{20}$ | $n_D^{20}$ | M. R. calcd. | M. R. obs. | Investigator |
|---|---|---|---|---|---|---|---|
| C=C—C—C—C—C | I | 63.4–63.7 | 0.6732 | 1.3858 | 29.44 | 29.33 | Present paper |
| | | 63.35 ± 0.05 | $.67875_4^{15}$ | $1.3885_D^{15}$ | 29.27 | $29.27_{H\infty}$ | v. Risseghem[a] |
| | | 64.5–65 | $.684^{14}$ | $1.393_D^{14}$ | 29.33 | 29.23 | Bourguel[b] |
| C=C—C—C—C<br>C | I | 53.6–54.0 | .6700 | 1.3835 | 29.44 | 29.31 | Present paper |
| C=C—C—C—C<br>C | I | 53.6–53.9 | .6646 | 1.3825 | 29.44 | 29.48 | Present paper |
| C<br>C=C—C—C<br>C | I | 41.2 | $.6549_4^{15}$ | $1.3766_D^{18}$ | 29.33 | 29.53 | Fomin–Sochanski[c] |
| C—C=C—C—C—C | II | 67.9–68.1 | .6813 | 1.3928 | 29.44 | 29.45 | Present paper |
| | | 68.0–68.2 | $.6863_4^{15}$ | $1.3981_D^{15}$ | 29.27 | $29.42_{H\infty}$ | v. Risseghem[d] |
| | | 67.7–68.1 | .66888 | 1.38319 | 29.325 | 29.307 | v. Beresteyn[e] |
| C—C=C—C—C<br>(H.B.) C | II | 57.7–58.5 | .6709 | 1.3885 | 29.44 | 29.61 | Present paper |
| | | 57–58.5 | .6706 | 1.3883 | 29.32 | 29.58 | Gorsky[f] |
| C—C=C—C—C<br>(L.B.) C | II | 54.2–55.2 | .6702 | 1.3881 | 29.44 | 29.61 | Present paper |
| C—C—C=C—C—C | II | 66.6–67.0 | .6816 | 1.3942 | 29.44 | 29.53 | Present paper |
| | | 64.0 | $.6807^{19}$ | $1.394_D^{19}$ | 29.44 | 29.52 | Lesp.–Wiem.[g] |
| C=C—C—C—C<br>C | III | 61.5–62.0 | .6817 | 1.3921 | 29.44 | 29.38 | Present paper |
| | | 64–66 | ... | .... | ... | ... | Brooks–Humph.[h] |
| C=C—C—C<br>C C | III | 56.0–56.5 | .6803 | 1.3995 | 29.44 | 29.33 | Present paper |
| | | 55.0–57.5 | ... | .... | ... | ... | |
| C=C—C—C<br>C—C | III | 66.2–66.7 | .6914 | 1.3990 | 29.44 | 29.41 | Present paper |
| | | 67–68 | .69403 | 1.40276 | 29.44 | 29.55 | Kon[i] |
| C—C=C—C—C<br>(H.B.) C | IV | 67.6–68.2 | .6956 | 1.4002 | 29.44 | 29.32 | Paul Flory[m] |
| | | 69.9–70.2 | $.7022_4^{15}$ | $1.4072_D^{15}$ | ... | 29.61 | v. Risseghem[j] |
| C—C=C—C—C<br>(L.B.) C | IV | 65.7–66.2 | .6940 | 1.3994 | 29.44 | 29.34 | Paul Flory[m] |
| | | 65.1–65.7 | $.7220_4^{15}$ | $1.3997_D^{15}$ | | | v. Risseghem[j] |
| C—C=C—C—C<br>C | IV | 67.2–67.5 | .6904 | 1.4005 | 29.44 | 29.56 | Present paper |
| | | 66.7–67.1 | $.69145_4^{15}$ | $1.4028_D^{5}$ | 29.44 | 29.674 | v. Risseghem[k] |
| C—C=C—C<br>C C | V | 73–74 | .7077 | 1.4248 | 29.44 | 29.32 | v. Risseghem[l] |

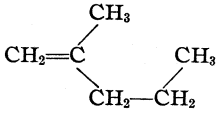
[a] Ref. 11 c. [b] Bourguel, *Bull. soc. chim.*, **41**, 1475 (1927). [c] Fomin and Sochanski, *Ber.*, **46**, 246 (1931). [d] Ref. 11 c, p. 333. [e] v. Beresteyn, *Bull. soc. chim. Belg.*, **25**, 293 (1911). [f] Gorsky, *J. Russ. Phys.-Chem. Soc.*, **42**, 1356 (1910). [g] Ref. 12 b. [h] Ref. 11 a, p. 831. [i] Kon, *J. Chem. Soc.*, **119**, 810 (1921). [j] v. Risseghem, *Bull. soc. chim. Belg.*, **31**, 213 (1922). [k] v. Risseghem, *ibid.*, **32**, 144 (1923). [l] v. Risseghem, *ibid.*, **30**, 9 (1921). [m] Flory and Boord, incomplete and unpublished work now being done in this Laboratory.

those of type III, 2,3-dimethyl-1-butene boils lower than 2-methyl-1-pentene. These facts lead to the conclusion that *branching in an alkyl group attached to an unsaturated carbon atom of an olefin tends to lower the boiling temperature.*

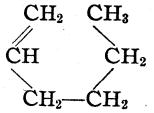
The above conclusion seems to stand in direct contradiction to a gen-

eralization made many years ago by Pawlow.[13] This author, having in mind the boiling points of tetramethylethylene and of the two dimethylethylethylenes, was led to observe that: "In the saturated compounds the accumulation of methyl groups in most cases lowers the boiling point, in hydrocarbons of the ethylene series, on the other hand, the same condition seems to be able to raise the boiling temperature." Pawlow failed to restrict his generalization to those olefins in which the methyl groups are bound directly to the unsaturated carbon atoms. Table I shows tetramethylethylene (2,3-dimethyl-2-butene) to be the highest boiling hexene. All the hexenes of type IV, having two methyl groups attached to unsaturated carbon, boil above 65°. The other hexenes boiling above this temperature include 2-hexene, 3-hexene and *unsym.*-diethylethylene (2-ethyl-1-butene). These facts stand in agreement with Pawlow's generalization, which may now be restated in a modified form: *the accumulation of methyl groups on the unsaturated carbon atoms of an olefin tends to raise the boiling point.* This conclusion seems to be supported by the fact that β-olefins always boil distinctly higher than α-olefins while (in so far as data are available) β-olefins also boil higher than γ-olefins.

Holding in mind both of the above conclusions one is tempted to make the broader generalization: *The more deeply the point of unsaturation is buried within the molecular structure the higher the boiling point;* or, conversely: *the more exposed the point of unsaturation the lower the boiling point.* The data available are probably not sufficient to justify so broad a generalization but as was previously pointed out *tert.*-butylethylene (3,3-dimethyl-2-butene) having both a highly branched alkyl group and an exposed double bond is the lowest boiling of all the hexenes; while tetramethylethylene (2,3-dimethylethylene) with its double bond completely submerged in the molecular structure is the highest boiling hexene. In the light of the above generalization it is interesting to observe that 2-methyl-1-pentene boils lower than 1-hexene and it is easily conceivable that in the average molecular configuration of the former (A) the point of unsaturation may be



A



B

more exposed than in the latter (B). It is also of interest to note that the boiling points of *sym.*-diethylethylene (3-hexene) and *unsym.*-diethylethylene (2-ethyl-1-butene) lie very close together.

In general the densities and the refractive indices of the hexenes follow the boiling points. *Tert.*-butylethylene is the lightest and the least refractive, while tetramethylethylene is the heaviest and has the highest re-

[13] Pawlow, *Ann.*, **196**, 126 (1879).

fractive power. It will be observed that for the hexenes of type I and for the β-hexenes of type II the density and the refractivity follow exactly the same order as the boiling point. For those of types III and IV the parallelism is not so marked but in general a high boiling point indicates high density and high refractive index.

*Cis–Trans* **Isomerism.**—Two isomeric forms have been found for both 3-methyl-2-pentene and 4-methyl-2-pentene. The former case has been carefully studied by Mlle. v. Risseghem,[14] using a large quantity of material. The low-boiling isomer was of doubtful purity since its density was unusually high and its molecular refractivity correspondingly low.

The data attributed to Flory and one of us on this compound are taken from incomplete and unpublished work now being done in this Laboratory on the application of the β-bromo ether synthesis to the olefins of type IV. The low-boiling isomer, as obtained by us, seems to correspond closely with that given by Mlle. v. Risseghem. The density and molecular refractivity are even more acceptable. Our high-boiling isomer does not correspond to the main fraction obtained by this investigator, but rather to a small intermediate fraction indicated in her distillation data. The data must be regarded as tentative and subject to verification as the investigation develops.

4-Methyl-2-pentene is described for the first time in the present paper. The amount of this hydrocarbon available was not sufficient for a completely detailed study and the purity of the low-boiling isomer was not wholly satisfactory. Its boiling point range covered an entire degree. The partition of each of these two hexenes into two isomeric forms is sufficiently definite, however, as to leave no possible doubt as to their separate existence.

The criteria which have been used for determining the true identity of the *cis* and *trans* forms in such a case have led to contradictory results. Wislicenus and his co-workers[15] regard the low-boiling isomer of 2-butene as the *cis* form. Pfeiffer[16] on the other hand believed the low-boiling to be the *trans* form, and Lucas and his co-workers[17] have chosen to agree with this point of view. Van de Walle and Henne,[18] working with the halogen substituted ethylenes and following the principles laid down by Michael,[19] found that the *trans* form was usually the low-boiling isomer. 1,2-Diiodoethylene was the only exception.

If it is true that that isomer having its double bond most deeply buried in

[14] Van Risseghem, *Bull. soc. chim. Belg.*, **31**, 213 (1922).
[15] Wislicenus, Talbot, Henze and Schmidt, *Ann.*, **313**, 207–250 (1900).
[16] Pfeiffer, *Z. physik. Chem.*, **48**, 58 (1904).
[17] Young, Dillon and Lucas, THIS JOURNAL, **51**, 2528 (1929).
[18] Van de Walle and Henne, *Bull. acad. roy. Belg.*, 360–374 (1925).
[19] Michael, *J. prakt. Chem.*, **46**, 222 (1892); **52**, 352 (1895).

the molecular structure has the highest boiling point, then one would expect this to be the *trans* isomer. The difference in boiling point between the two isomeric forms of 3-methyl-2-pentene is 4.5–4.8° (v. Risseghem) and of 4-methyl-2-pentene is 3.0–3.4°.

Should the above point of view prove to be justifiable, one may find here a possible explanation for the apparent non-existence of *cis–trans* isomerism in the case of 2-hexene and 3-hexene. Since in such a case the double bond would be about equally exposed in the *cis* and the *trans* configurations the boiling points would lie very close together, requiring more refined fractionation than has been possible up to the present time.

**Criteria of Purity.**—In a critical study of the simple olefins one finds the usual criteria for purity of doubtful value. Many olefins are readily subject to isomerization and polymerization. All of them tend to form azeotropic mixtures. The products obtained usually boil over a range of temperatures. In the present investigation, with a single exception, the purified products have been obtained with a boiling range of less than 0.5°. Since all olefins have the same composition, ultimate analysis does not reveal impurities due to admixture with isomers or polymers.

A comparison of the observed with the calculated molecular refractivities is also frequently used as an index of purity. It should be pointed out that while this method would reveal any considerable admixture with polymer it would be wholly ineffectual in a mixture of isomers. Columns five and six (Table I) show the observed and calculated refractivities of the hexenes. The measurements are for the sodium D-line except as otherwise indicated. The experimentally determined values, in general, are in better agreement with 29.44, the calculated value based on Eisenlohr's constants, than with 29.325, the value when Brühl's constants are used. It has long been known that many unsaturated compounds show anomalous molecular refractivity. This anomaly is especially characteristic of compounds containing conjugated double bonds. Since the physical constants of the hexenes vary so widely with the position of the double bond in the molecular structure, one is led to doubt whether the double bond should be given the same weighting in all types of simple olefins.

## Experimental Part

**α-Chloro Ethers.**—The α-chloro ethers were prepared by the method previously described. α-Chloroethyl-[1a] and α-chloro-*n*-propyl ethyl ether[1c] were obtained in 89 and 70% yields, respectively.

**α-Chloro-isobutyl ethyl ether,** $(CH_3)_2CHCHClOC_2H_5$, which it seems has not been previously described, was obtained in 90% (crude) yield, b. p. 43° (24 mm.), $d_4^{20}$ 0.9316, $n_D^{20}$ 1.4130, M. R. calcd., 36.42, M. R. observed, 36.46.

*Anal.* Calcd. for $C_6H_{13}OCl$: Cl, 25.97. Found: Cl, 25.09.

**α,β-Dibromo Ethers.**—The dibromo ethers used in the present investigation were prepared by three different methods. α,β-Dibromoethyl- and α,β-dibromo-*n*-propyl

ethyl ethers, prepared as described in previous communications,[1b,c] were obtained in 95 and 94% (crude) yields, respectively.

**α,β-Dibromo-isobutyl-ethyl ether,** $(CH_3)_2CBrCHBrOC_2H_5$, was prepared by an analogous method in 92% yield, b. p. 88–89° (22 mm.), $d_4^{20}$ 1.5671, $n_D^{20}$ 1.4450, M. R. calcd. 48.08, M. R. observed 44.20.

*Anal.* Calcd. for $C_6H_{12}OBr$: Br, 61.49. Found: Br, 60.29.

**α,β-Dibromo-*m*-butyl methyl ether,** $CH_3CH_2CHBrCHBrOCH_3$, was prepared by a modification of the method of Späth and Göhring.[20] One mole of *n*-butyraldehyde was cooled and mixed with an excess of cold methyl alcohol. This solution was brominated at 0° using one molar quantity of bromine. The mixture was saturated with hydrogen bromide and the lower layer of α,β-dibromo-*n*-butyl methyl ether was separated. The crude product was placed over anhydrous calcium chloride and the volatile impurities removed under diminished pressure. The crude dibromo ether was used without further purification.

The third method of preparing α,β-dibromo ethers consisted in adding bromine to the α,β-unsaturated ethers of the type described by Lauer and Spielman.[4] These authors have shown that the β-bromo ethers, described by Swallen and one of us, react with powdered potassium hydroxide with the loss of hydrogen bromide, forming the unsaturated ethers indicated above.

The required β-ethoxy-*n*-propyl bromide and β-ethoxy-*n*-butyl bromide were prepared as previously described in yields of 71 and 75%, respectively. Each of these β-bromo ethers was placed in a three-necked iron flask[21] and mixed with twice its weight of finely powdered anhydrous potassium hydroxide. The flask was provided with an iron stirrer having a mercury seal and thirty or forty one-half inch iron balls (ball bearings) were also added to aid in breaking up the salt incrustations as the reaction proceeded. The generator was provided with a Hempel distilling column which in turn was attached to an efflux condenser and a thermometer so arranged as to indicate the boiling point of the distillate. The flask was jacketed with asbestos paper and heated over an electric hot-plate. The effluence of the unsaturated ether was practically completed in three to four hours. The temperature was then raised to drive over the last portions. The receiver was protected from the moisture of the air by a calcium chloride tube and the product collected over a small amount of solid potassium hydroxide. In spite of all precautions the product always contained a small amount of the corresponding ketone and some unchanged β-bromo ether. It was separated from the latter by fractionation. No attempt was made to remove the trace of ketone.

By the above procedure β-ethoxy-*n*-propyl bromide was made to yield 83% of 2-ethoxypropene,[4] b. p. 61–63° (748 mm.), $d_4^{20}$ 0.7712, $n_D^{20}$ 1.3915, M. R. calcd. 26.44, M. R. observed 26.55, and β-ethoxy-*n*-butyl bromide to yield 70% of 2-ethoxy-1-butene,[22] b. p. 84–87° (7.45 mm.), $d_4^{20}$ 0.7848, $n_D^{20}$ 1.4018, M. R. calcd. 31.16, M. R. observed 31.03. These values agree well with those previously recorded.

One mole of the 2-ethoxy olefin was dissolved in 500 cc. of anhydrous ether, the solution cooled to −10° and one mole of pure dry bromine added slowly. The mixture was stirred during the bromination, the product being protected from the moisture by a calcium chloride tube. If the temperature is maintained below −5° the product will be quite colorless. No attempt was made to isolate the dibromo ether but the ethereal solution was converted at once by condensation with the appropriate Grignard reagent

[20] Späth and Göhring, *Monatsh.*, **41**, 319 (1920).

[21] This flask was kindly loaned to us by Dr. G. Bryant Bachman of this Department. It gave excellent service.

[22] Faworski, *J. prakt. Chem.*, [2] **37**, 533 (1888).

into the desired β-bromo ether. In this manner 2-ethoxypropene and 2-ethoxy-1-butene were converted into 1,2-dibromo-2-ethoxypropane and 1,2-dibromo-2-ethoxy-*n*-butane, respectively.

**β-Bromo-α-ethoxyhexanes.**—The Grignard solutions used in the present investigation were prepared and evaluated by the method described by Gilman and his co-workers.[23] The condensations to form the β-bromo ethers were carried out by the procedure indicated by Shoemaker and one of us. It has been observed in the present work that a 10 to 30% excess of Grignard reagent is desirable. Furthermore the best results are obtained by stirring the reaction mixture from ten to fifteen hours after the addition is completed. The condensations are best made in dilute solution. Table II gives the physical constants and analyses of the ten β-bromo-α-ethoxyhexanes used in the present investigation.

TABLE II

β-BROMO-α-ETHOXYHEXANES

| Name | B. p., °C. (mm.) | $d_4^{20}$ | $n_D^{20}$ | M. R. obs. Calcd., 48.55 | Analysis, Br, % Calcd. | Found |
|---|---|---|---|---|---|---|
| 1-Bromo-2-ethoxyhexane[a] | 86.5 (19) | 1.1488 | 1.4485 | 48.71 | 38.23 | 37.99 |
| 1-Bromo-2-ethoxy-4-methylpentane[b] | 85.0 (25) | 1.1468 | 1.4455 | 48.50 | 38.23 | 38.25 |
| 1-Bromo-2-ethoxy-3-methylpentane | 74.75 (13) | 1.1682 | 1.4503 | 48.08 | 38.23 | 38.28 |
| 2-Bromo-3-ethoxyhexane | 73.0 (12) | 1.1455 | 1.4474 | 48.71 | 38.23 | 38.22 |
| 2-Bromo-3-ethoxy-3-methylpentane | 79.5 (25) | 1.1377 | 1.4458 | 49.13 | 38.23 | 38.12 |
| 4-Bromo-3-methoxyhexane | 65–66 (12) | 1.2378 | 1.4495 | 42.32 | 40.97 | 40.76 |
| 1-Bromo-2-ethoxy-2-methylpentane | 81–82 (19) | 1.1706 | 1.4532 | 48.29 | 38.23 | 38.20 |
| 1-Bromo-2-ethoxy-2,3-dimethylbutane | 78–79 (15) | 1.1671 | 1.4560 | 48.71 | 38.23 | 38.12 |
| 1-Bromo-2-ethoxy-2-ethylbutane | 79–81 (17) | 1.1758 | 1.4548 | 48.29 | 38.23 | 37.97 |
| 2-Bromo-3-ethoxy-2-methylpentane[c] | 65–67 (20) | 0.9557 | 1.4376 | ... | 38.23 | |

[a] Swallen and Boord, THIS JOURNAL, **52**, 655 (1930). [b] Dykstra, Lewis and Boord, *ibid.*, **52**, 3401 (1930). [c] This compound was not pure and did not yield to purification.

**Preparation of the Hexenes.**—The β-bromo ethers described above were converted into the corresponding hexenes by the action of zinc dust on the alcoholic solution as previously indicated. From 50 to 100 g. of the bromoethoxyhexane (or in one case bromomethoxyhexane) was dissolved in 125 to 175 cc. of *n*-propyl alcohol and 35 to 75 grams of zinc dust added. The mixture was refluxed at the incipient boiling temperature for ten to fifteen hours. The contents of the flask were then submitted to distillation. Distillation began near the boiling point of the azeotropic mixture of the alcohol and olefin and gradually rose to that of the pure alcohol. By the time the latter temperature had been reached all the olefin had distilled. The distillate was diluted with twice its volume of cold water and the upper olefinic layer separated. The hexene was washed four or five times with an equal volume of cold water and dried over granular calcium chloride. The olefin was then distilled over metallic sodium to remove the last traces of alcohol and water.

Table III shows the starting materials and the yield obtained in each step of the synthesis. The last column of this table also shows the "over all" yield of hexene based on the aldehyde. The boiling points, densities, refractive indices and molecular refractivities of the hexenes prepared in the present investigation are shown in Table I.

**Dibromohexanes.**—For the purpose of analysis and characterization, each of the above hexenes was converted into the corresponding dibromohexane. Ten grams of the olefin was dissolved in 50 cc. of chloroform and the solution cooled to 0°. An equivalent amount of pure dry bromine also dissolved in 50 cc. of chloroform was slowly added. The temperature of the reaction mixture was maintained below 5°, and the reaction

[23] (a) Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1576 (1929); (b) Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).

TABLE III

YIELD VALUES BY STEPS IN THE HEXENE SYNTHESES

| Hexene | Aldehyde | R—Mg—Br | I α-Chloro ether | II Di-bromo ether | III β-Bromo ether | IV Olefin | Unsatd. ether | Total yield on aldehyde |
|---|---|---|---|---|---|---|---|---|
| 1-Hexene | Acet- | *n*-Butyl | 89 | 95 | 78 | 78 | .. | 51.4 |
| 4-Methyl-1-pentene | Acet- | Isobutyl | 89 | 95 | 48 | 57 | .. | 23.1 |
| 3-Methyl-1-pentene | Acet- | *s*-Butyl | 89 | 95 | 30 | 72 | .. | 18.3 |
| 2-Hexene | Propion- | *n*-Propyl | 70 | 94 | 60 | 75 | .. | 29.6 |
| 4-Methyl-2-pentene | Propion- | Isopropyl | 70 | 94 | 55 | 70[a] | .. | 25.35 |
| 3-Hexene | *n*-Butyr- | Ethyl | .. | .. | 68 | 85 | .. | |
| 2-Methyl-1-pentene | Acet- | Methyl | 89 | 95 | 71 | .. | 83 | |
| | | *n*-Propyl | (2-ethoxypropene) | ? | 55 | 65 | .. | 17.8 |
| 2,3-Dimethyl-1-butene | Acet- | Methyl | 89 | 95 | 71 | .. | 83 | |
| | | Isopropyl | (2-ethoxypropene) | ? | 48 | 70 | .. | 16.7 |
| 2-Ethyl-1-butene | Acet- | Ethyl | 89 | 95 | 75 | .. | 70 | |
| | | Ethyl | (2-ethoxy-1-butene) | ? | 55 | 58 | .. | 14.2 |
| 2-Methyl-2-pentene | Isobutyr- | Ethyl | 90 | 92 | 49 | 40 | .. | 16.2 |

[a] This number represents the total yield including both forms. Of this amount fifty parts were obtained as the high boiling form and twenty parts as the low boiling form. This is equivalent to a total yield on the basis of the aldehyde and of 18.1 and 7.25% of the high and low boiling forms, respectively.

carried out in diffused light. The chloroform was distilled off and the dibromide distilled under diminished pressure. The yields were approximately quantitative.

The physical constants and analyses of the dibromohexanes are shown in Table IV.

TABLE IV

DIBROMOHEXANES

| Name | B. p., °C. (mm.) | $d_4^{20}$ | $n_D^{20}$ | M. R. obs. | M. R. Calcd. 45.44 | Br, %, found | Br, %, Calcd. 65.53 |
|---|---|---|---|---|---|---|---|
| 1,2-Dibromohexane[a,b] | 89–90 (18) | 1.5774 | 1.5024 | 45.62 | | 65.59 | |
| 1,2-Dibromo-3-methylpentane | 99 (30) | 1.6016 | 1.5060 | 44.90 | | 65.42 | |
| 1,2-Dibromo-4-methylpentane[1b] | 87 (21) | 1.5689 | 1.4980 | 45.62 | | 65.41 | |
| 2,3-Dibromohexane[b,c] | 90 (16) | 1.5812 | 1.5025 | 45.62 | | 65.46 | |
| 2,3-Dibromo-4-methylpentane | 78 (22) | 1.5996 | 1.5070 | 45.38 | | 65.24 | |
| | | (from high-boiling isomer) | | | | | |
| 2,3-Dibromo-4-methylpentane | 72–73 (18) | 1.5983 | 1.5060 | 45.37 | | 65.38 | |
| | | (from low-boiling isomer) | | | | | |
| 3,4-Dibromohexane[d] | 80–81 (13) | 1.6027 | 1.5045 | 45.14 | | 65.38 | |
| 1,3-Dibromo-2-methylpentane | 87–88 (20) | 1.5581 | 1.5015 | 46.11 | | 64.38 | |
| 1,2-Dibromo-2,3-dimethylbutane | 80 (17) | 1.6033 | 1.5105 | 45.58 | | 64.75 | |
| 1,2-Dibromo-2-ethylbutane[e] | 87 (21) | 1.6045 | 1.5112 | 45.60 | | 65.12 | |
| 2,3-Dibromo-2-methylpentane[f] | 71–72 (18) | 1.5849 | 1.5063 | 45.62 | | 65.33 | |

[a] Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926). [b] V. Risseghem, *Bull. soc. chim. Belg.*, **35**, 328 (1926). [c] Klarfeld, *Monatsh.*, **26**, 84 (1905). [d] Lespieau and Wiemann, *Bull. soc. chim.*, **48**, 627 (1929). [e] Kon, *J. Chem. Soc.*, **119**, 810 (1921). [f] Jawein, *Ann.*, **195**, 255 (1879).

## Summary

The nuclear synthesis of olefins through the β-bromo ethers has been used in a systematic survey of the hexenes. Ten of the thirteen structurally possible members of this family have been prepared, including those previously unknown. The method is shown to be applicable to the synthesis of monoalkyl, symmetrical and unsymmetrical dialkyl ethylenes. It is believed the method will ultimately prove applicable also to the trialkyl and tetraalkyl ethylenes.

The confusion which has existed in the physical constants of the olefins is beginning to disappear. A definite relation is shown to exist between the physical properties and molecular structure of the hexenes. Certain rules have been formulated relating the boiling points, densities and refractive indices of the hexenes to their structure.

Eight bromohexyl ethyl ethers, three hexenes and five dibromohexanes are herein described for the first time.


COLUMBUS, OHIO

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[CONTRIBUTION NO. 72 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

# STUDIES OF POLYMERIZATION AND RING FORMATION. X. THE REVERSIBLE POLYMERIZATION OF SIX-MEMBERED CYCLIC ESTERS

BY WALLACE H. CAROTHERS, G. L. DOROUGH AND F. J. VAN NATTA

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Reactions leading to the formation of high polymers have received considerable attention during the past few years both because of their inherent interest as representatives of a realm that has been relatively little explored, and because of their bearing on the formulation of naturally occurring macromolecular materials. In this connection the behavior of six-membered cyclic esters is of peculiar interest: they combine with themselves, in many cases spontaneously at the ordinary conditions, to form polymers of high molecular weight, and this transformation is reversible. Since these esters are generally free from unsaturation, their self-combination must have its origin in some peculiarity of the heterocyclic system. Six-membered heterocycles are quite common among naturally occurring materials and are closely associated with natural polymers (sugars and polysaccharides, diketopiperazines and polypeptides); it is therefore reasonable to assume that the behavior of the cyclic esters lies closer to the natural processes that result in the formation of macromolecular substances than does the polymerization of unsaturated compounds, such as styrene, which have been more extensively studied.

Several isolated examples of the reversible polymerization of six-mem-

bered cyclic esters have been recorded in the literature but the question of the mechanism of this phenomenon has received very little attention. In the present paper, we report some observations bearing on this point.

**Previous Work.**—Fichter and Beisswenger[1] first reported that "δ-valerolactone (I) is characterized by a remarkable and surprising phenomenon: it polymerizes after a short time; the initially mobile oil becomes gradually thicker and finally solidifies to a crystalline mass." The polymer after recrystallization melted at 47–48°. Attempts to determine its molecular weight gave values ranging from a five- to a seven-fold polymer. Later the same transformation was observed by Hollo,[2] who also records the spontaneous polymerization of the lactone (II) of hydroxyethylglycolic acid.

Bischoff and Walden[3] in 1893 described the transformation of glycolide (III) under the influence of heat or a trace of zinc chloride into a polymeric solid melting at 220°. On being distilled in a vacuum it was reconverted to the monomer, melting at 86–87°.

Drew and Haworth[4] have obtained the lactone (IV) of 2,3,4-trimethyl-*l*-arabonic acid in crystalline form (m. p. 45°) and observed that, in the presence of traces of hydrogen chloride, it is converted into a crystalline polymeric powder which has a considerably higher melting point, a lower solubility, and a lower specific rotation than the monomer. Its molecular weight (about 2000) indicates that it is derived from about ten molecules of the monomer. At 175° it distils completely *in vacuo*, and the distillate consists of pure lactone. Drew and Haworth[5] favored a linear polyester structure for this polymer.

Trimethylene carbonate (V) was first described by Carothers and Van Natta.[6] The monomer is a very soluble crystalline solid melting at 47°. If it is heated to 130° for a few minutes with a trace of potassium carbonate, the mobile melt suddenly becomes very viscous and evolves a small amount of gas. The colorless, viscous sirup on cooling solidifies to a stiff mass which shows an apparent molecular weight of about 4000. When this mass is heated in a vacuum it distils almost quantitatively, and the distillate consists of pure monomer.

Monomeric ethylene oxalate (VI) was first described by Bischoff and Walden,[7] who obtained it as a crystalline solid melting at 143° by distilling the product of the action of ethylene glycol on monoethyl oxalate.

[1] Fichter and Beisswenger, *Ber.*, **36,** 1200 (1903).

[2] Hollo, *ibid.*, **61,** 895 (1928).

[3] Bischoff and Walden, *ibid.*, **26,** 262 (1893).

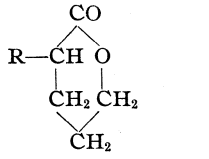
[4] Drew and Haworth, *J. Chem. Soc.*, 775 (1927).

[5] *Cf.* Haworth, "The Structure of Sugars," Edward Arnold and Co., London, 1929, p. 78.

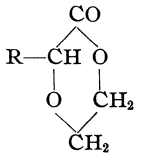
[6] Carothers and Van Natta, THIS JOURNAL, **52,** 314 (1930).

[7] Bischoff and Walden, *Ber.*, **27,** 2939 (1894).

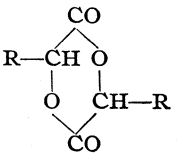
Later Bischoff[8] obtained less soluble, higher melting forms of ethylene oxalate, and showed that these on distillation were converted into the 143° form. Bischoff also observed that the melting points of the ethylene oxalates change on standing, and suspected that these changes might be due to a reversible polymerization, but he reported no comparative molecular weight data. The relation of the various forms of ethylene oxalate to one another has lately been studied by Carothers, Arvin and Dorough.[9] It was found that the flat, diamond-shaped crystals of the monomer completely disintegrate during the course of a few days, yielding a microcrystalline powder which consists of a mixture of polymers. From this mixture by careful extraction with cold solvents two definite fractions can be isolated. One of these melts at 159° and has an apparent molecular weight of about 3000; the other fraction,which is probably much more highly polymeric, melts at 173° and is too insoluble for molecular weight determinations. These isolated fractions on standing lose their identity: they revert spontaneously within a few days to more complicated mixtures which usually contain appreciable amounts of monomer. The polymeric ethylene oxalates can be converted into the monomer (with considerable loss) by vacuum distillation. Propylene oxalate (VIa) (m. p. 142°) is converted by the action of heat into an insoluble, microcrystalline polymer melting at 178°.[9]



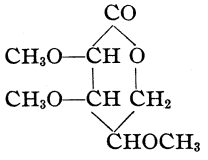
I, R = H
Ia, R = $n$-$C_3H_7$



II, R = H
IIa, R = $C_2H_5$



III, R = H
IIIa, R = $CH_3$



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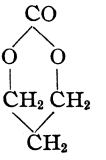
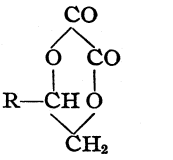
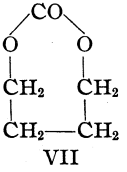


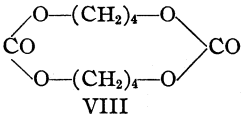
V



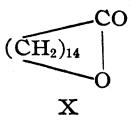
VI, R = H
VIa, R = $CH_3$



VII



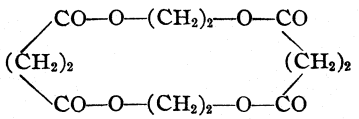
VIII



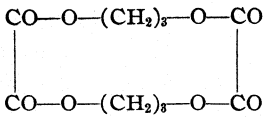
X

[8] Bischoff, *Ber.*, **40**, 2803 (1907).

[9] Carothers, Arvin, and Dorough, THIS JOURNAL, **52**, 3292 (1930); *cf.* Bergmann and Wolff, *J. prakt. Chem.*, **128**, 229 (1930); and Carothers and Van Natta, *Ber.*, **64**, 1755 (1931).



IX



XI

**Generality of the Phenomenon.**—The examples cited above show that the capacity to undergo reversible polymerization is quite common among six-membered cyclic esters. The presence of substituent groups, however, has a considerable effect and, in general, a depressing effect, on this tendency. The unsubstituted esters I, II and VI polymerize spontaneously at ordinary temperature in the complete absence of any added catalyst; substituted esters on the other hand, such as Ia, IIa, IV and VIa, require the action of heat, or catalysts, or both, and in some cases polymerization fails altogether.

A number of substituted δ-valerolactones (I) have been described in the literature, but without any record of their polymerization. We have therefore prepared α-*n*-propyl-δ-valerolactone (Ia) as described in the experimental part. Although δ-valerolactone was found to be completely polymerized to a waxy solid after twenty-nine days at room temperature, the new α-*n*-propyl-δ-valerolactone was still unchanged after twelve months, nor did it show any signs of polymerization after being heated to 80° for one month. However, when heated to 80° for one month in the presence of a trace of potassium carbonate or zinc chloride, it became more viscous, and its apparent molecular weight rose to 1100–1200.

Hollo[2] records the spontaneous polymerization of the lactone (II) of hydroxyethylglycolic acid, but makes no mention of the polymerization of its α-alkyl derivatives (II, R = $C_2H_5$, *n*-$C_3H_7$ and *iso*-$C_3H_7$) which he prepared at the same time. We have made attempts to polymerize the lactone (IIa) of hydroxyethyl-α-hydroxybutyric acid. Sixteen hours of heating at 140–160° failed to produce any change in the viscosity or the color of the pure lactone. Under the same conditions in the presence of a trace of potassium carbonate, only a slight increase in viscosity occurred.

Bischoff and Walden[10] state that lactide (IIIa) does not polymerize under the conditions that result in the polymerization of glycolide (III). We find, however, that at 250–275° the polymerization of lactide is quite rapid: in two hours a sample was transformed into a resinous mass which showed an apparent molecular weight of about 3000. A similar effect can be obtained at much lower temperatures, *e. g.*, 140–150°, if potassium carbonate is present.

We have also examined some of the higher homologs of lactide. The cyclic esters derived from α-hydroxycaprylic and from α-hydroxypalmitic

[10] Bischoff and Walden, *Ann.*, **279**, 71 (1894).

acids were prepared and heated for various periods both in the presence and absence of catalysts. Evidences of polymerization could be found only at temperatures sufficiently high to produce considerable decomposition.

Finally, it may be mentioned that although ethylene oxalate polymerizes spontaneously at the ordinary temperature, propylene oxalate undergoes a similar transformation only at considerably elevated temperatures.[9]

**Peculiarity of the Phenomenon.**—Among cyclic esters the capacity to undergo reversible polymerization in the manner illustrated by the examples cited above is peculiar to six-membered rings. The γ-lactones and other five-membered cyclic esters show no tendency to polymerize, and no corresponding polymers are known. Thus, we have heated samples of pure γ-butyrolactone both with and without catalysts (zinc chloride, potassium carbonate) at 80° for twelve months; none of the samples showed any detectable increase in viscosity. We have also made various attempts to polymerize ethylene carbonate, but these attempts were all unsuccessful, although the corresponding six-membered ring, trimethylene carbonate (V), is readily polymerized.[11]

It appears also that cyclic esters of more than six members show no tendency to polymerize spontaneously. Information on this point is somewhat incomplete. No aliphatic cyclic esters of nine to thirteen atoms have been described. In fact no practical means for the preparation of such esters are yet known. In general, the attempt to prepare cyclic esters of more than six atoms from open chain compounds leads to linear polymers.

Thus the six-atom ring trimethylene carbonate (V) is readily obtained by heating diethyl carbonate with trimethylene glycol, and subsequently distilling the product *in vacuo*, but when diethyl carbonate is similarly treated with tetramethylene glycol, the product is a polymeric material that is not capable of being distilled *in vacuo*, *i. e.*, it cannot be depolymerized; only at temperatures above 300°, it undergoes complete thermal decomposition and yields a complicated mixture of products among which are found very small amounts of the dimeric fourteen-membered ring VIII.[6] Attempts to detect the presence of the monomer VII have been unsuccessful. Similar behavior is observed with trimethylene oxalate[9] and ethylene succinate.[12] The preparation of these esters leads to linear polymeric products of high molecular weight. No smooth depolymeriza-

[11] β-Lactones have not been specifically examined from this standpoint, but it appears likely in view of some observations recorded by Johansson [Lunds Universitets Ärsskrift II, [2] **12**, 3 (1916)] that simple lactones of this class undergo irreversible polymerization under the action of heat.

[12] Carothers and Dorough, THIS JOURNAL, **52**, 711 (1930).

tion of these polymers can be effected by the action of heat; but at high temperatures they undergo complete thermal decomposition, yielding a complicated mixture of gaseous, liquid and tarry products containing very small amounts of the cyclic dimers which are, respectively, fourteen and sixteen-membered rings (XI and IX). The corresponding monomers have never been obtained.

The following observations indicate the relatively great stability of the large cyclic esters. Specimens of dimeric trimethylene oxalate (XI), dimeric ethylene succinate (IX), and exaltolide (X) have been preserved in the laboratory for two years without showing any signs of change. The last two of these compounds have been heated in sealed tubes at 170° for a considerable period of time. After twelve hours they were quite unchanged; after forty-three hours they had become slightly colored and their melting points slightly lowered, but signs of appreciable polymerization were absent.[13]

The peculiar position of the six-membered esters is shown in the following outline, in which, for simplicity, the starting material in each case is represented as an hydroxy acid.

(A) The structural unit is five atoms long

$$\mathrm{HO{-}R{-}COOH} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} \mathrm{[O{-}R{-}CO]}$$

(B) The structural unit is six atoms long

$$\begin{array}{l} \mathrm{HO{-}R{-}COOH} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} \mathrm{[O{-}R{-}CO]} \\ \quad +H_2O \uparrow \downarrow -H_2O \qquad\qquad \uparrow\downarrow \\ \cdots\mathrm{{-}O{-}R{-}CO{-}O{-}R{-}CO{-}O{-}R{-}CO{-}O{-}R{-}CO{-}}\cdots \end{array}$$

(C) The structural unit is more than six atoms long

$$\begin{array}{l} \mathrm{HO{-}R{-}COOH} \\ \quad +H_2O \uparrow \downarrow -H_2O \\ \cdots\mathrm{{-}O{-}R{-}CO{-}O{-}R{-}CO{-}O{-}R{-}CO{-}O{-}R{-}CO{-}}\cdots \end{array}$$

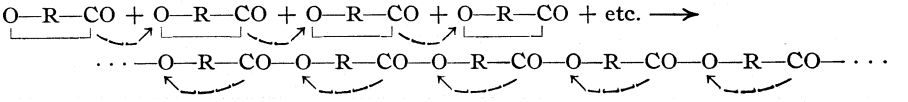
Under B it should be mentioned that the reversible relation between the monomer and the polymer complicates the problem of deciding in a given case which of these is the real primary product of the dehydration of the hydroxy acid. In any event the conditions of the dehydration

[13] We do not intend to suggest that the polymerization of large cyclic esters is impossible. In fact, since such esters can be hydrolyzed to the corresponding hydroxy acids, it is evident from equation C that such a polymerization can probably be effected under some conditions. The process would consist in hydrolysis of the cyclic ester to the hydroxy acid and the dehydration of this to the polyester. Both of these steps might occur in a single operation under appropriate conditions, *e. g.*, at elevated temperature in the presence of a small amount of water plus mineral acid. But the experiments described above do demonstrate that the large cyclic esters, at least qualitatively, are very different from the six-membered esters.

usually favor the polymerization of the monomer, so that the latter is isolated only by vacuum distillation of the actual reaction product. Dietzel and Krug[14] have presented evidence to show that the self-esterification of lactic acid leads directly only to polylactyl lactic acids and that lactide, when it is produced, results from the depolymerization of these poly esters. On the other hand, it is established, at least in certain instances,[4] that δ-lactones may be formed as such directly from the corresponding hydroxy acid. No doubt in most cases, depending upon the conditions, either the monomer or the polymer may be formed as the primary product.

Under C it should be mentioned that although attempts to prepare seven-membered cyclic esters from dibasic acids and dihydric alcohols lead only to poly esters, ε-hydroxy acids appear to be dehydrated with the simultaneous formation of polymer and monomer.[15] There is, however, no record of the interconversion of these two forms, and the higher ω-hydroxy acids yield linear polymers exclusively.[16]

**Mechanism of the Phenomenon.**—The smooth reversibility of the polymerization of the six-membered cyclic esters and the absence of double-bond unsaturation at first suggested that here, if anywhere, might be found the missing models of that hypothetical phenomenon, association polymerization, to which for a time the peculiarities of natural polymers were widely attributed.[17] This thought was considerably weakened, however, when Dr. J. W. Hill presented in the closely analogous case of adipic anhydride, a direct and decisive proof of the structural difference between monomer and polymer.[18] No similar proof is possible in the esters under consideration; nevertheless, all the evidence together conclusively favors the mechanism suggested by Carothers and Van Natta,[6] namely, that the polymers are linear polyesters and that both the polymerization and its reversal proceed by a process of ester interchange. This is indicated in the equation




[14] Dietzel and Krug, *Ber.*, **58**, 1307 (1925).

[15] Marvel and Birkheimer, THIS JOURNAL, **51**, 260 (1929); Blaise and Koehler, *Compt. rend.*, **148**, 1773 (1909).

[16] No exception to this statement has been observed among the numerous esters we have prepared from dibasic acids and glycols, but we have lately found that in the self-esterification of ω-hydroxydecanoic acid in the absence of solvent, appreciable amounts of the cyclic dimeric ester are formed. This has already been prepared by a different method and described by Lycan and Adams [THIS JOURNAL, **51**, 3450 (1929)].

[17] Abderhalden, *Naturwissenschaften*, **12**, 716 (1924); Bergmann, *ibid.*, **13**, 1045 (1925); Pringsheim, *ibid.*, **13**, 1084 (1925); Hess, *Ann.*, **435**, 1 (1924).

[18] Hill, THIS JOURNAL, **52**, 4110 (1930).

The peculiar position occupied by the six-membered cyclic esters may be explained, as we have already suggested,[6] by stereochemical factors: rings of six atoms are strained (or may pass through positions of strain); rings of five atoms or more than ten atoms are strainless. In the cyclic esters the strain can be relieved by the process of ester interchange, which results in polymerization. The resulting polymers (from the six-membered esters) are easily depolymerized owing to the high probability of the close approach of atoms six atoms apart in a chain. Polyesters whose depolymerization would result in larger monomeric rings are not depolymerized; the probability of the close approach of the requisite atoms is too slight.

The interchange mechanism for the polymerization of the six-membered esters is supported by the following facts: (1) The polymers have the same apparent analytical compositions,[19] and saponification equivalents as the corresponding monomers, and they yield the same products on hydrolysis.

(2) The products of the polymerization of the six-membered cyclic esters closely resemble in their physical properties the polymers formed by the action of dibasic acids on glycols, or by the self-esterification of the higher $\omega$-hydroxy acids. It has been definitely established that these polymers are linear polyesters; the chains are open and are terminated by hydroxyl and/or carboxyl groups.[12,20]

(3) Both the forward and the reverse transformations are catalyzed by acids and bases, typical ester-interchange catalysts.

(4) The speed of the polymerization runs parallel with the susceptibility to hydrolysis. The much greater susceptibility of $\delta$-lactones to hydrolysis as compared with analogous $\gamma$-lactones is well known. The hydrolysis constant for $\delta$-valerolactone (I) is more than twice that of its $\alpha$-methyl derivative,[2] and the former polymerizes spontaneously while the latter does not. Similar relations hold for the lactone of hydroxyethylglycolic acid (II) and its $\alpha$-alkyl derivatives.[2] The hydrolytic constants for glycolide in its two stages are, respectively, 0.0179 and 0.119, while the corresponding values for lactide are 0.00313 and 0.0611.[21] The former polymerizes much more readily than the latter. Ethylene oxalate, which polymerizes with extraordinary facility, is so sensitive to hydrolysis that, like an acid, it can be titrated directly with moderately warm dilute alkali.

**Further Observations.**—Data on some polymers of $\delta$-valerolactone are presented in Table I.

[19] But the values for carbon are usually somewhat low and the values for hydrogen somewhat high. This may signify that the chains are open, or it may mean merely that the polyesters in spite of the fact that they are insoluble in water are nevertheless somewhat hygroscopic and difficult to dry.

[20] Lycan and Adams, THIS JOURNAL, **51**, 625, 3450 (1929).

[21] Johansson and Sibelius, *Ber.*, **52**, 745 (1919).

TABLE I

POLYMERS OF δ-VALEROLACTONE

| No. | Catalyst | Temp. during polym., °C. | Time | M. p. of polymer, °C. | Mol. wt. of polymer (boiling point in benzene) | |
|---|---|---|---|---|---|---|
| 1 | None | Room | 29 days | 35–40 | 1060 | 1060 |
| 2 | None | 80–85 | 13 days | 52–53 | 1270 | 1330 |
| 3 | $K_2CO_3$ | 80–85 | 5 days | 53–54 | 1840 | 1820 |
| 4 | $ZnCl_2$ | 80–85 | 5 days | 52–54 | 2230 | 1846 |
| 5 | None | 150 | 10 hrs. | 52–55 | 2110 | 2240 |
| 6 | Over $CH_3COCl$ | Room | 3 days | 50–51 | 1720 | 1720 |

The melting points are in general somewhat higher than those reported by Fichter and Beisswenger.[1] The polymer is soluble in a variety of organic solvents and is readily crystallized, *e. g.*, from a mixture of petroleum ether and benzene. When allowed to solidify from a melt it forms an opaque, soft, waxy solid. The crystals are poorly developed; they appear under the microscope as tiny irregular particles.

Polymeric δ-valerolactone is acidic. In acetone solution it can be titrated with alkali to a sharp end-point which persists for several minutes. Sample 5 of Table I thus showed a neutral equivalent of 2153 and 2243 in two determinations. The closeness of this value to the observed molecular weights indicates the probable presence of one carboxyl group for each molecule. It is not quite certain that this agreement is not accidental. A product prepared by heating the monomer at 175° showed an equivalent weight of 6320 and a molecular weight of about 1500 (observed 1420 and 1660), but the molecular weight values are under suspicion because of severe foaming. It seems certain however that at least part of the polyester molecules bear carboxyl groups.

The polymeric δ-valerolactone is not homogeneous, but contains molecules of different sizes. Its sodium salts are not soluble in water. A sample of recrystallized polymer formed at ordinary temperature (m. p. 53–56°) showed by titration in acetone an equivalent weight of 3160. The acetone solution was evaporated and the resulting dry sodium salt taken up in hot absolute alcohol, filtered and cooled to crystallize. In this way fractions of different solubilities and sodium content were isolated: (1) 0.38 g. containing 0.22% Na; (2) 0.77 g. containing 0.49% Na; (3) 0.14 g. containing 3.92% Na. The equivalent weights inferred from the sodium contents are: (1) 10,400, (2) 4700, (3) 590. Determination of the molecular weight of fraction 2 by the boiling point in benzene gave the value 3880.

The polyester derived from the lactone (II) of hydroxyethylglycolic acid differs in its behavior from polymeric δ-valerolactone. It cannot be titrated to a sharp end-point with 0.1 *N* alkali. Attempts to prepare a sodium salt by treating it with sodium bicarbonate under various condi-

tions have led to mixtures from which two distinct fractions are readily separated. One of these is unchanged polyester entirely free of sodium; the other is the pure sodium salt of hydroxyethylglycolic acid. Thus even so mild an alkali as sodium bicarbonate hydrolyzes the polyester, and it is impossible to determine whether the polymeric molecules bear carboxyl groups. Ethylene oxalate (VI) shows a still more exaggerated sensitivity to alkalies. Trimethylene carbonate (V) appears to be neutral. In this case any terminal carboxyl groups that might arise during the polymerization would be lost spontaneously since they would be linked to oxygen (R—O—CO—OH). The momentary liberation of a small amount of gas at the end of the sudden thermal polymerization of trimethylene carbonate is perhaps due to loss of carbon dioxide from acid carbonic ester groups formed in this way.

For δ-valerolactone, however, as already indicated, the presence of a terminal carboxyl group in the polymeric molecule is fairly clearly demonstrated.

It seems likely that the first step in the polymerization of the cyclic esters involves the intervention of a trace of the corresponding hydroxy acid or one of its derivatives. One can imagine that hydroxyvaleric acid would thus react with valerolactone

$$HO(CH_2)_4COOH + O(CH_2)_4CO \longrightarrow HO(CH_2)_4CO—O(CH_2)_4COOH$$

The dimeric acid would then react in the same manner with valerolactone to form a trimeric acid, and the reaction would continue in this sense until all of the lactone was exhausted or the chains became too long for further reaction. In this mechanism a foreign acid might equally well participate, and it would be bound in the product as the first unit of the polymeric chain. Experiments in this direction were made with chloroacetic acid.

One gram of δ-valerolactone was heated with 0.1 g. of chloroacetic acid for fifteen hours at 150–160°. The reaction mixture, which solidified on standing in a refrigerator, was recrystallized from alcohol and carefully dried. It melted at 42° and contained 3.28% chlorine. It was triturated with an excess of sodium bicarbonate in the presence of a little water, and the product after drying was extracted with warm alcohol. The polyester which separated was thrice recrystallized from alcohol. It now melted at 45–46° and contained 2.3% sodium. The molecular weights calculated respectively from the chlorine and sodium content, assuming a molecule having the formula XII, are 1008 and 1000.

(XII) $$ClCH_2CO—[O(CH_2)_4CO—]_xOH$$

In a similar experiment in which one gram of valerolactone was heated with 0.05 g. of chloroacetic acid the initial product melted at 48° and contained 2.06% chlorine. The sodium salt melted at 50–51° and contained 1.35% sodium. The molecular weights calculated from these data are 1720 and 1705.

Chlorine-containing derivatives were also obtained by heating the polymeric lactone with chloroacetic acid. Two grams of polymer and 0.1 g. of chloroacetic acid were heated for ten hours at 150–160°. The product was thrice crystallized from alcohol. It contained 1.75% chlorine, and this corresponds to a molecular weight of 2030. Its neutral equivalent as indicated by titration with alkali was 2083.

These results are at least consistent with the mechanism suggested above. A mechanism involving the mutual coalescence of two molecules of monomer to form a twelve-atom ring and the growth of this through the progressive absorption of more monomeric molecules seems less likely, but some observations lately made in this Laboratory on the polymerization of cyclic anhydrides indicate that this mechanism is not at all impossible.

**Lactone (II) of Hydroxyethylglycolic Acid.**—Preparation: The method of Hollo[2] was slightly modified. The crude mixture containing the sodium salt of the hydroxy acid, sodium chloride and a little glycol was washed with acetone, suspended in absolute alcohol and treated with less than the calculated amount of hydrochloric acid. The precipitated sodium chloride was removed by filtration and the lactone isolated from the filtrate by distillation. In this way it was readily obtained free of chlorine.

When allowed to stand it gradually solidified to a pasty mass. After five weeks the solid was crystallized five times from ethyl acetate. It then melted at 62–64° and showed a molecular weight in boiling benzene of about 460 (observed, 451, 471). This probably corresponds approximately with Hollo's polymer melting at 56–63°.

A polymer formed by heating the lactone at 150° for five hours after being crystallized four times from ethyl acetate melted at 87–89°. It was very soluble in cold chloroform, hot ethyl acetate and hot alcohol, slightly soluble in ether, cold ethyl acetate and water. Molecular weight determinations in boiling benzene gave the values 1647 and 1788.

Hollo describes another type of polymer obtained when the sodium salt of the hydroxy acid is treated with an excess of hydrochloric acid. This melts at 66–68°, boils at 216 to 220°, and distils without change at atmospheric pressure.

It seems quite impossible however that a polymer should boil only 5° higher than the monomer (210–215°), and the explanation of Hollo's observation probably lies in the fact that the hydrochloric acid present in the polymer distils with the monomer during depolymerization and the polymerization of the distillate is so powerfully catalyzed that it occurs very rapidly. In our experiments a specimen of polymeric lactone originating from a preparation in which a slight excess of hydrochloric acid was used to liberate the hydroxy acid was observed to distil at 215–216° and the distillate solidified immediately on cooling. The solid product after three crystallizations from ethyl acetate melted at 85 to 87°.

This polymer distilled completely, but the distillate was not unchanged polymer. Molecular weight determinations on the distillate made immediately after the completion of the distillation gave the values, 144, 140 and 121 (calcd. for monomer, 102). After two hours the distillate had already begun to crystallize. After twenty-four hours it had solidified, and the solid after recrystallization thrice from ethyl acetate showed a molecular weight of about 900 in boiling benzene (observed, 867, 931).

Polymers originating from preparations in which an excess of hydrochloric acid was carefully avoided behaved in precisely the same way except that the reversion of the distillate was much slower; it remained fluid for twenty-four hours. The melting points of the purified polymers obtained from either source approached 89°.

**α-*n*-Propyl-δ-valerolactone** was prepared through the steps indicated in the following equations.

$$C_6H_5OCH_2CH_2CH_2Br + n\text{-}C_3H_7CH_2(COOC_2H_5)_2 \longrightarrow$$
$$C_6H_5OCH_2CH_2CH_2(C_3H_7)C(COOC_2H_5)_2 \text{—} HBr \longrightarrow BrCH_2CH_2CH_2CH(C_3H_7)COOH$$
$$\longrightarrow BrCH_2CH_2CH_2CH(C_3H_7)COONa \longrightarrow \underline{OCH_2CH_2CH_2CH(C_3H_7)CO}$$

Phenoxypropyl-(*n*-propyl)-malonic diethyl ester: colorless liquid, b. p. (4 mm.) 195–200°; $d_4^{26}$ 1.0246; $n_D^{25}$ 1.4820.

*Anal.* Calcd. for $C_{10}H_{20}O_5$: C, 67.85; H, 8.33. Found: C, 68.60, 68.04; H, 8.03, 8.09.

δ-Bromo-α-*n*-propylvaleric acid: b. p. (5 mm.) 148–150°; $d_4^{20}$ 1.3851, $n_D^{20}$ 1.4730.

*Anal.* Calcd. for $C_8H_{15}O_2Br$: C, 43.05; H, 6.72; neutral equivalent, 223. Found: C, 44.33; H, 6.84; neutral equivalent, 220, 222

The high values for carbon are probably due to the presence of some phenol.

α-*n*-Propyl-δ-valerolactone: b. p. (10 mm.) 118–120°; $d_4^{20}$ 0.9929; $n_D^{20}$ 1.4585.

*Anal.* Calcd. for $C_8H_{14}O_2$: C, 67.67; H, 9.85; saponification equivalent, 142. Found: C, 67.59, 67.50; H, 10.01, 10.18; saponification equivalent, 143, 144.

**Preparation of Lactide.**—The preparation of lactide by methods described in the older literature[22] gave poor yields, but excellent results were obtained by the following method based on recent patents.[23] Two hundred grams of commercial lactic acid was heated at ordinary pressure in a Claisen flask by a metal bath at 120° until water ceased to distil. The temperature was then raised to 140° and the pressure reduced to 10 mm. During six hours water continued to distil slowly from the flask. The pressure in the system was reduced to 5 mm. and the temperature raised sufficiently to cause rapid distillation of the lactide, which solidified in the receiver. The yield of crude product was 125 g. It was purified by crystallization from ether; m. p. 128°.

## Summary

Several isolated examples of the reversible polymerization of six-membered cyclic esters have been briefly reported in the literature. Further examples are reported in the present paper, together with some experimental data and speculations on the mechanism of the phenomenon. The following conclusions are reached.

1. The ability to undergo reversible polymerization is generally characteristic of six-membered cyclic esters.
2. Ester rings of five atoms or more than six atoms do not polymerize under the action of heat.
3. The tendency of six-membered cyclic esters to polymerize is closely related to their great susceptibility toward hydrolysis; both tendencies are diminished by the presence of substituent groups.
4. The polymers formed from six-membered cyclic esters are linear polyesters and, at least in certain instances, the chains are open and terminated by hydroxyl and carboxyl groups.
5. Both the polymerization and the depolymerization consist essentially in a process of ester interchange.
6. The peculiar position occupied by the six-membered cyclic esters is readily explained by stereochemical considerations based on the Sachse–Mohr theory.

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[22] Gay-Lussac and Pelouze, *Ann.*, **7**, 43 (1833); Bischoff and Walden, *Ber.*, **26**, 263 (1893).

[23] Chemische Werke, French Patent 456,824 (1913); Grüter and Pohl, U. S. Patent 1,095,205 (1914).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE WM. S. MERRELL CO.]

# STUDIES OF GLYCIDOL. III. REACTIONS WITH ACID CHLORIDES[1]

BY T. H. RIDER

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Earlier papers in this series have described the preparation of glycidol[2] and its reactions with secondary amines.[3] The reaction with these amines was found to proceed according to the equation

$$\underset{\diagdown O \diagup}{CH_2—CH}CH_2OH + NHR_2 = R_2NCH_2CHOHCH_2OH$$

the amino group always assuming the alpha position. In the reaction of glycidol with acid chlorides two modes of addition are possible, and both are found to occur.

$$\underset{\diagdown O \diagup}{CH_2—CH}CH_2OH + RCOCl = \underset{\displaystyle OCOR}{\underset{|}{CH_2CHCl}}CH_2OH \qquad (I)$$

$$\underset{\diagdown O \diagup}{CH_2—CH}CH_2OH + RCOCl = CH_2Cl\underset{\displaystyle OCOR}{\underset{|}{CH}}CH_2OH \qquad (II)$$

It is obvious that in the presence of an excess of acid chloride, monochlorohydrin di-esters will be formed. Thus, glycidol when treated with a slight excess over two moles of acetyl chloride gave a mixture of $\alpha$- and $\beta$-monochlorohydrin diacetate. Alcoholysis of this mixture yielded a mixture of $\alpha$- and $\beta$-monochlorohydrins in which both isomers were detected by the preparation and separation of their phenylurethans according to the method given in the first paper of this series. It would be of interest to determine the percentage of the two isomeric products resulting from the reactions of glycidol with a series of acid chlorides. This might be accomplished by alcoholysis of the resulting esters and a study of the resulting monochlorohydrin mixture by the physical chemical method described by Smith.[4] This is not entirely feasible, however, since the alcoholysis and subsequent distillation of the monochlorohydrin mixture entail about a 15% loss of material, and it is impossible to assume that the ratio of $\alpha$- and $\beta$-isomers is comparable to that in the original esters.

The reactions of glycidol with *p*-nitrobenzoyl chloride have been accorded somewhat more attention due to the interest attached to the resulting esters as intermediates for the production of local anesthetics. A

[1] A portion of the material in this paper is taken from the thesis presented by T. H. Rider to the Faculty of the Graduate School of Yale University in candidacy for the Degree of Doctor of Philosophy, June, 1928.

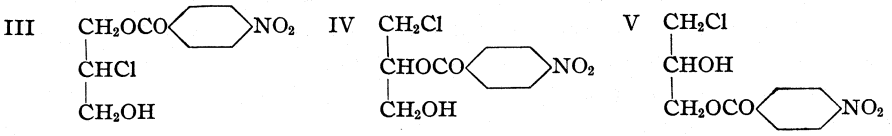
[2] Rider and Hill, THIS JOURNAL, **52**, 1521 (1930).

[3] Rider with Hill, *ibid.*, **52**, 1528 (1930).

[4] Smith, *Z. physik. Chem.*, **92**, 717 (1918); *ibid.*, **93**, 59 (1919); *ibid.*, **94**, 723 (1920).

nitrobenzoate chlorohydrin ester, by reaction with a suitable amine and subsequent reduction of the nitro group, would yield an aminobenzoic acid ester of an amino alcohol whose structure would be analogous to that of novocaine.

The reaction between glycidol and *p*-nitrobenzoyl chloride according to reactions I and II would yield the two products III and IV.




A third ester (V) isomeric with these two can be obtained by the action of *p*-nitrobenzoyl chloride on monochlorohydrin. In the latter reaction it is to be assumed that only the one product will result since the alpha hydroxyl will react preferentially, while it is obviously impossible that the direct addition of *p*-nitrobenzoyl chloride to glycidol could yield this same product. The mononitrobenzoates of monochlorohydrin resulting from these two reactions appear, however, to be identical at least in so far as boiling point is concerned. Therefore the chances for separating these isomers by fractional distillation is nil.

When two proportions of the acid chloride are used, and the di-esters formed, it is obvious that mono esters IV and V will yield identical di-esters, while III will yield an isomeric di-ester. These two di-esters have been described previously by Fairbourne and Foster,[5] and suggested by them as the basis of a method of detecting $\alpha$- and $\beta$-monochlorohydrins in a mixture. They treated the chlorohydrin with two molecular proportions of *p*-nitrobenzoyl chloride in chloroform solution using quinoline as an acceptor for the hydrogen chloride formed. The reaction mixture was taken up in ether, washed with water, dilute sulfuric acid, sodium bicarbonate solution, again with water and dried over sodium sulfate. After drying they removed the solvents and reported that a quantitative yield of monochlorohydrin di-*p*-nitrobenzoate was obtained in this manner.

This work was not overlooked, as suggested by Fairbourne,[6] at the time the writer published as co-author the method for the detection of the isomeric chlorohydrins by means of their phenylurethans, but the method could not be duplicated. In the progress of this later work the difficulty was discovered. The isomeric monochlorohydrin di-*p*-nitrobenzoates are insoluble in ether, although their crystallization from ether is retarded by traces of chloroform. When Fairbourne and Foster's method was again repeated, the desired product was found not in the dried ether solution, but as a solid precipitate mixed with the drying agent,

[5] Fairbourne and Foster, *J. Chem. Soc.*, 3148 (1926).

[6] Fairbourne, Gibson and Stephens, *ibid.*, 445 (1931).

from which it could be isolated by digestion with water. No doubt if the drying period were curtailed, a fairly large percentage of the ester still would be retained in solution. The writer has prepared glycerol α-monochlorohydrin di-*p*-nitrobenzoate by an alternative method with success, and has found that one method of purification consists in dissolving the product in chloroform, treating with norite, filtering, diluting with ether and allowing it to crystallize out slowly. The product purified in this way melted at 108–109° uncorr. (Fairbourne and Foster reported m. p. 107–108°).

The writer, in agreement with the earlier work of Fairbourne and Foster, finds that the mixed di-*p*-nitrobenzoates of the α- and β-chlorohydrins melt at decidedly lower temperatures, although he has not, as yet, isolated sufficient of the pure β-isomer (m. p. 121–122°) for accurate analysis. Such a mixture of the isomeric di-esters results from the action of two molecular proportions of *p*-nitrobenzoyl chloride on glycidol.

## Experimental

**The Action of Acetyl Chloride on Glycidol (Monochlorohydrin Diacetate).**—Three hundred grams of acetyl chloride is placed in a three-necked round-bottomed flask equipped with a mechanical stirrer, an efficient reflux condenser and a dropping funnel. The acetyl chloride is brought to the boiling point, the heating stopped and 100 g. of glycidol allowed to drop slowly into the reaction mixture during stirring. After the addition is complete, the solution is heated for several hours to insure completion of the reaction and the excess acetyl chloride removed. The residue is now transferred to a Claisen bulb and distilled. Under a pressure of 0.4–0.6 mm., monochlorohydrin diacetate distils at 96.5–97° (102–105° at 6 mm.). The yield is 69%.

*Anal.* Calcd. for $C_7H_{11}O_4Cl$: Cl, 18.25. Found: Cl, 18.58, 18.66.

**The Alcoholysis of Monochlorohydrin Diacetate.**—The diacetate is refluxed with five times its weight of absolute methyl alcohol containing dry hydrogen chloride. After heating for six hours, the excess alcohol and methyl acetate are removed and the residue of glycerol monochlorohydrin is distilled (b. p. 81° at 0.5 mm.). The yield is 81–85%.

*Anal.* Calcd. for $C_3H_7O_2Cl$: Cl, 32.09. Found: Cl, 32.07, 31.91.

The presence of both α- and β-isomers was detected by the preparation and separation of their phenylurethans as described in the first paper of this series.

**The Action of *p*-Nitrobenzoyl Chloride on Glycidol (Ratio 1:1).**—92.8 g. of *p*-nitrobenzoyl chloride and 37 g. of glycidol are mixed in ether solution and refluxed for ten hours. The ether must be strictly anhydrous or two by-products will be formed in large quantities, namely, *p*-nitrobenzoic acid anhydride (m. p. 188°), and monochlorohydrin. The ether is removed and the residue distilled, collecting the fraction from 197–217° at 1 mm. This material redistils from 205–207° at 0.8 mm. The yield is 70–75%.

*Anal.* Calcd. for $C_{10}H_{10}O_5NCl$: N, 5.4; Cl, 13.7. Found: Cl, 13.6, 13.5; N, 5.2, 5.3.

**The Action of *p*-Nitrobenzoyl Chloride on Glycerol α-Monochlorohydrin (Ratio 1:1).**—Fifty-nine grams *p*-nitrobenzoyl chloride, 35 g. of glycerol α-monochlorohydrin and 50 g. (slight excess) of diethylaniline are mixed in ether solution and allowed to stand at room temperature. After two weeks a layer of light yellow oil has separated on the

bottom of the flask together with crystals of diethylaniline hydrochloride. The latter forms a complete layer between the ether and oil phases, so that the ether can be decanted. After washing out the hydrochloride crystals with water, the oil becomes ether soluble. If the reaction is run in hot benzene using pyridine instead of diethylaniline as the acceptor for hydrogen chloride the results are entirely similar, *i. e.*, an oil separates but redissolves in the benzene upon the addition of water. The ether or benzene solution is washed with dilute hydrochloric acid, sodium carbonate solution, water and dried over sodium sulfate. The solvent is removed and the residue distilled. A fraction collected from 225–260° at 1.5 mm. redistils from 202–205° at 0.2 mm. and at 207° under a pressure of 1.5 mm. The yields are 60–65%.

*Anal.* Calcd. for $C_{10}H_{10}O_5NCl$: N, 5.4; Cl, 13.7. Found: N, 5.2, 5.5; Cl, 13.5, 13.4.

**The Action of *p*-Nitrobenzoyl Chloride on Glycidol (Ratio 2:1).**—The first molecular proportion of *p*-nitrobenzoyl chloride is combined with glycidol as described above, and the resulting ethereal solution treated with a second molecular proportion of the acid chloride and slightly more than an equivalent amount of pyridine as acceptor for the hydrogen chloride. After refluxing for several hours to insure completion of the reaction, the ethereal solution is washed with dilute hydrochloric acid, sodium bicarbonate solution and water and dried over anhydrous sodium sulfate. The solution is filtered and the ether evaporated. Any solid material obtained from the ether solution[7] is added to the drying agent and the combined solids extracted with a small amount of chloroform. The chloroform is filtered and mixed with five volumes of anhydrous ether. On standing the mixed di-*p*-nitrobenzoates of α- and β-monochlorohydrin are precipitated. This mixture melts at 97–98°. The yield is 85% of the theoretical.

*Anal.* Calcd. for $C_{17}H_{13}O_8N_2Cl$: N, 6.86; Cl, 8.7. Found: N, 6.6; Cl, 8.5, 8.8.

**The Action of *p*-Nitrobenzoyl Chloride on Glycerol α-Monochlorohydrin (Ratio 2:1).**—6.86 g. of *p*-nitrobenzoyl chloride is dissolved in enough pyridine to give a clear solution at room temperature; 2.7 g. of α-monochlorohydrin is added and the mixture allowed to stand for several days. The pyridine solution is then thrown into an excess of cold dilute hydrochloric acid and the solid di-*p*-nitrobenzoate is thrown out in 93–96% yield. The melting point of this crude solid is 105°. This product is dried, dissolved in a small amount of chloroform, treated with norite, filtered and a large volume of anhydrous ether added. After standing for two days the di-*p*-nitrobenzoate of α-monochlorohydrin has completely precipitated. This product melts at 108–109°. The yield is 96%.

*Anal.* Calcd. for $C_{17}H_{13}O_8N_2Cl$: N, 6.86; Cl, 8.7. Found: N, 6.48, 6.52; Cl, 8.6, 8.7.

## Summary

The actions of *p*-nitrobenzoyl chloride on glycidol and on glycerol α-monochlorohydrin and the products resulting therefrom are described. The di-*p*-nitrobenzoate of glycerol α-monochlorohydrin is insoluble in ether, contrary to previous indications in the literature.

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[7] Although the products are ether insoluble, they do not tend to precipitate from the ether solution until the last traces of pyridine have been washed out. Crystallization is then slow enough so that no material is lost before the ether solution is placed over the drying agent.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# NITRO AND AMINO TRIPHENYLGUANIDINES[1]

BY ELIZABETH DYER AND TREAT B. JOHNSON

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The present investigation was undertaken in order to prepare a series of amino derivatives of triphenylguanidine for pharmacological use in a coöperative study of the chemotherapy of tuberculosis. Hesse has shown[2] that the only organic compounds, so far examined, which inhibit the growth of tubercle bacilli are basic in character. Inasmuch as the aminotriphenylguanidines should possess high basicity, it was suggested by Professor Hesse that the study of the bactericidal power of this type of compound be incorporated in our systematic study of tuberculosis chemotherapy.

The preparation of some aminotriphenylguanidines, as well as the pharmacological results obtained in Professor Hesse's experiments, are described in Section D. Inasmuch as the amino compounds were prepared from the corresponding nitro derivatives, it was necessary to develop adequate methods of synthesizing the latter, which are discussed in Sections B and C.

The preparation of the nitrotriphenylguanidines involved, first, the synthesis of a series of thioureas.

**A. Preparation of Thioureas.**—The nitroarylthioureas were prepared by the addition of an aniline derivative to an isothiocyanate. A study of this reaction has revealed the inactivity of *p*-nitraniline, in many cases, toward isothiocyanates with which aniline combines at once. For example, *p*-nitraniline could not be made to combine with phenyl isothiocyanate. This result confirms a similar observation by Losanitsch.[3] Moreover, *p*-nitraniline reacted with *p*-nitrophenyl isothiocyanate only in the presence of pyridine as a catalyst, whereas aniline combined quickly and quantitatively with the same isothiocyanate in the absence of catalysts. On the other hand, the reaction between *p*-nitraniline and benzoyl isothiocyanate took place with ease, giving the desired thiourea derivative.

The three *p*-nitrophenylarylthioureas prepared in the above ways have not been previously described. There is in the literature, however, a confusion of the known di-*m*-nitrophenylthiourea with the previously unknown di-*p*-nitrophenylthiourea. Brückner,[4] in 1873, reported the preparation of di-*p*-nitrophenylthiourea, melting at 161°. Later work by

[1] Constructed from a dissertation presented by Elizabeth Dyer to the Faculty of the Graduate School of Yale University in June, 1931, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Meissner and Hesse, *Arch. Exp. Path. Pharm.*, **147**, 339 (1930); Hesse and Meissner, *ibid.*, **159**, 679 (1931).

[3] Losanitsch, *Ber.*, **14**, 2365 (1881).

[4] Brückner, *ibid.*, **6**, 1103 (1873).

three independent investigators[5] showed that di-*m*-nitrophenylthiourea melted at 161°, and indicated that the corresponding para derivative had never been prepared. Loh and Dehn,[6] in 1926, referring to the early article by Brückner, assumed that a di-nitrophenylthiourea obtained by them, and which melted at 161°, was the para derivative. The above evidence indicates that their compound was probably di-*m*-nitrophenylthiourea.

**B. Preparation of Nitrotriphenylguanidines.**—Two nitro derivatives of triphenylguanidine are described in the literature, namely, *m*-nitrophenyldiphenylguanidine[7,8] and tri-*m*-nitrophenylguanidine.[8] Both substances were prepared by methods involving desulfurization of thioureas. The procedures used, however, resulted in low yields of the guanidines due to the formation of several by-products.

In the present investigation more successful methods of preparing nitrotriphenylguanidines have been developed. The most satisfactory of these consists in the use of a mixture of iodine and pyridine to destroy hydrogen sulfide during interaction of thiourea and amine

$$RNHCSNHR' + R''NH_2 + I_2 + 2C_5H_5N \longrightarrow R''N{=}C(NHR)NHR' + 2C_5H_5N{\cdot}HI + S$$

Former investigators have described the use of either iodine[8,9] or pyridine[10] alone as desulfurizing agents in the preparation of guanidines, but the combination of these two reagents has previously been applied only to the synthesis of thioureas.[11] A summary of the results obtained by the application of this procedure to the preparation of *p*-nitrotriphenylguanidines is given in Table I.

TABLE I

PREPARATION OF *p*-NITROTRIPHENYLGUANIDINES

| | Thioureas used | Amines used | Guanidines formed | Yield, % |
|---|---|---|---|---|
| 1 | $C_6H_5NHCSNHC_6H_4NO_2$[a] | $NH_2C_6H_5$ | $C_6H_5N{=}C(NHC_6H_5)NHC_6H_4NO_2$ | 80 |
| 2 | $CS(NHC_6H_4NO_2)_2$ | $NH_2C_6H_5$ | $C_6H_5N{=}C(NHC_6H_4NO_2)_2$ | 85 |
| 3 | $CS(NHC_6H_4NO_2)_2$ | $NH_2C_6H_4NO_2$ | $NO_2C_6H_4N{=}C(NHC_6H_4NO_2)_2$ | 73 |
| 4 | $C_6H_5NHCSNHC_6H_4NO_2$ | $NH_2C_6H_4NO_2$ | (a) $NO_2C_6H_4N{=}C(NHC_6H_5)NHC_6H_4NO_2$ | 34 |
| | | | (b) $NO_2C_6H_4N{=}C(NHC_6H_4NO_2)_2$ | 30 |
| 5 | $CS(NHC_6H_5)_2$ | $NH_2C_6H_4NO_2$ | (a) $NO_2C_6H_4N{=}C(NHC_6H_5)NHC_6H_4NO_2$ | 4 |
| | | | (b) $NO_2C_6H_4N{=}C(NHC_6H_4NO_2)_2$ | 3 |

[a] Nitro group in *p*-position.

A consideration of the table shows that reactions 1, 2 and 3 were satisfactory for the preparation of *p*-mononitro-, *p*-dinitro- and *p*-trinitro derivatives of triphenylguanidine, respectively. In the first two cases the reaction was practically instantaneous when a hot pyridine solution of

[5] Losanitsch, *Ber.*, **15**, 470 (1882); Steudemann, *ibid.*, **16**, 550 (1883); Fry, THIS JOURNAL, **35**, 1541 (1913).

[6] Loh and Dehn, *ibid.*, **48**, 2958 (1926).

[7] Brückner, *Ber.*, **7**, 1236 (1874).

[8] Losanitsch, *ibid.*, **16**, 49 (1883).

[9] Hofmann, *ibid.*, **2**, 456 (1869).

[10] Raffo, *et al.*, *Chemical Abstracts*, **8**, 2683 (1914); **12**, 1170 (1918).

[11] Fry, THIS JOURNAL, **35**, 1543 (1913).

the thiourea and amine was treated with an equivalent of iodine. In the third case the reaction was complete after the mixture had been boiled for four hours.

Reactions 4 and 5 did not proceed in a single direction. In the case of reaction 4, nearly half of the product consisted of the trinitrotriphenylguanidine (b) in addition to the expected dinitrotriphenylguanidine (a). Evidence as to the mechanism of the formation of the trinitrotriphenylguanidine was furnished by one experiment in which di-*p*-nitrophenylthiourea was isolated from the reaction mixture. If this substance is assumed to be the precursor of the trinitrotriphenylguanidine, the formation of the latter may be represented as:

$$C_6H_5NHCSNHC_6H_4NO_2 \longrightarrow [NO_2C_6H_4NCS] \xrightarrow[NO_2C_6H_4NH_2]{} CS(NHC_6H_4NO_2)_2 \xrightarrow[NO_2C_6H_4NH_2]{} NO_2C_6H_4N{=}C(NHC_6H_4NO_2)_2$$

Reaction 5 resulted in the formation of dinitro- and trinitrotriphenylguanidines in small yields instead of the mononitrotriphenylguanidine expected. It may be assumed that the mechanism of this reaction is analogous to that of reaction 4.

A second method of preparing nitrotriphenylguanidines consisted in the condensation of phenylisocyandichloride with nitranilines. This method, originally used by Sell and Zierold, and developed by Nef, Hantzsch and Johnson,[12] was successfully applied in the present investigation to the preparation of di-*p*-nitrophenylphenylguanidine and di-*m*-nitrophenylphenylguanidine.

A third means of obtaining nitrotriphenylguanidines was the condensation of alkyl pseudothioureas with the necessary aniline derivatives.[13] Although this reaction was investigated in the preparation of various nitrotriphenylguanidines, a good yield (70% of calcd.) was obtained in one case only, namely, by the action of aniline on S-methyl-*p*-nitrophenylphenylpseudothiourea.

**C. The Isomerism of the Di-*p*-nitrophenylphenylguanidines.**—Two di-*p*-nitrophenylphenylguanidines have been obtained, which melt at 168–169° and 191–193°, respectively. The methods of preparing these substances and the relationships between them are shown in Table II.

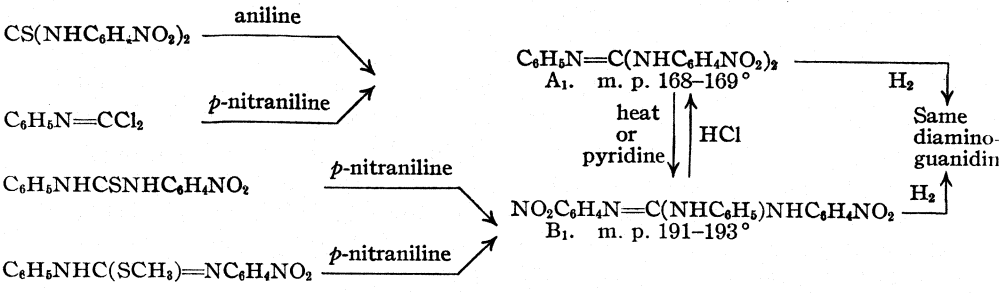
It is to be noted that the chemical differences in the methods of preparation, and the varying behavior of the two substances toward such agents as heat, pyridine or acids, exclude the possibility that the two forms are polymorphic varieties. The type of isomerism exhibited by these substances may be interpreted (1) as desmotropism, in which the compounds

[12] Sell and Zierold, *Ber.*, **7**, 1231 (1874); Nef, *Ann.*, **270**, 283 (1892); Hantzsch and Mai, *Ber.*, **28**, 982 (1895); Johnson and Chernoff, THIS JOURNAL, **34**, 166 (1912).

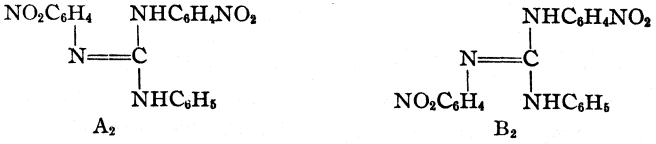
[13] Bernthsen and Friese, *Ber.*, **15**, 567 (1882).

TABLE II

ISOMERIC DI-*p*-NITROPHENYLPHENYLGUANIDINES




are represented by formulas $A_1$ and $B_1$, or (2) as geometrical isomerism, in which the configurations may be represented by formulas $A_2$ and $B_2$




The reactions by which the substances were prepared furnish evidence in support of formulas $A_1$ and $B_1$, as shown in Table II. The assignment of formulas $A_2$ and $B_2$ to the compounds would necessitate the assumption of a shift in the position of the double bond in both reactions, resulting in the formation of the substance melting at 168–169°. On the other hand, the ease of interconversion of the two guanidines is comparable to that of geometrical isomers.

Both isomers, when reduced catalytically, yielded the same amino compound. The possibility that the double bond in the guanidine nucleus may have been reduced as well as the nitro group seems very unlikely, since this linkage is ordinarily resistant to reduction.[14] Since the reduction was a vigorous exothermic reaction, it might be assumed that isomerization of one form to the other was brought about by the action of heat.

The formation of these two structural isomers of di-*p*-nitrophenylphenylguanidine is of interest in view of numerous previous attempts to demonstrate the existence of isomerism of this type among guanidine derivatives. Huhn's results,[15] which reported the isolation of two pairs of desmotropic varieties of triarylguanidines, were later discredited by Marckwald.[16] Likewise, Forster[17] and Schenck[18] obtained only *one* form of each of the guanidines studied, although two were theoretically possible.

[14] Thiele, *Ann.*, **273**, 133 (1893).
[15] Huhn, *Ber.*, **19**, 2404 (1886).
[16] Marckwald, *Ann.*, **286**, 343 (1895).
[17] Forster, *ibid.*, **175**, 56 (1875).
[18] Schenck, *Z. physiol. Chem.*, **77**, 328 (1912).

**D. Aminotriphenylguanidines.**—The aminotriphenylguanidines were obtained by catalytic reduction of the corresponding nitro compounds. The results of this research are summarized in Table III.

TABLE III

PREPARATION OF AMINOTRIPHENYLGUANIDINES

| | Nitro compound used | Amino compound produced | Yield, % |
|---|---|---|---|
| 1 | *p*-$C_6H_5N$=$C(NHC_6H_5)NHC_6H_4NO_2$ | *p*-$C_6H_5N$=$C(NHC_6H_5)NHC_6H_4NH_2$ | 69 |
| 2 | *p*-$C_6H_5N$=$C(NHC_6H_4NO_2)_2$ | *p*-$C_6H_5N$=$C(NHC_6H_4NH_2)_2$ or | 61–78 |
| 3 | *p*-$NO_2C_6H_4N$=$C(NHC_6H_5)NHC_6H_4NO_2$ | *p*-$NH_2C_6H_4N$=$C(NHC_6H_5)NHC_6H_4NH_2$ | |
| 4 | *m*-$C_6H_5N$=$C(NHC_6H_4NO_2)_2$ | *m*-$C_6H_5N$=$C(NHC_6H_4NH_2)_2$ | 80–90 |
| 5 | *p*-$NO_2C_6H_4N$=$C(NHC_6H_4NO_2)_2$ | *p*-$NH_2C_6H_4N$=$C(NHC_6H_4NH_2)_2$ | 66 |

The reduction took place most readily in the case of tri-*p*-nitrophenylguanidine (Expt. 5), least readily in the case of *p*-nitrophenyldiphenylguanidine (Expt. 1). It should be noted that the two isomeric di-*p*-nitrophenyl phenylguanidines yielded the same aminoguanidine (Expts. 2 and 3).

Both the nitro and amino derivatives of triphenylguanidine prepared in this investigation were sent for pharmacological study to Professor Erich Hesse, at the Institute for Pharmacology and Experimental Therapy at the University of Breslau. The nitro compounds were found to be entirely inactive toward the tubercle bacilli, a result which is in accord with Hesse's theory of the relation between the basicity of organic compounds and their bactericidal effect.[2] Contrary to expectations, the aminoguanidine derivatives, which we have prepared, likewise have been shown by Hesse[19] to possess no bactericidal activity. Hesse found, after an exhaustive study of many different types of guanidine derivatives, that the only representative of this series which retarded the growth of the tubercle bacillus *in vivo* was a tri-*p*-ethoxyphenylguanidine of unknown constitution. This was supplied for his researches by the I. G. Farbenindustrie, Hochst in Germany. It will be of especial interest to examine the behavior of several of the possible alkoxy substituted guanidines and also to study the effect of varying the structure of the alkoxy grouping.

## Experimental Part

***p*-Nitrophenyl Isothiocyanate.**—The isothiocyanate was prepared in 65–85% yields by treating thiophosgene with *p*-nitraniline. Coghill and Johnson's method[20] was modified by the use of two additional equivalents of *p*-nitraniline as hydrogen chloride acceptor. A mixture of 20 g. of thiophosgene with 72 g. of *p*-nitraniline suspended in 800 cc. of dry benzene was boiled for one hour with frequent shaking. The mixture was then cooled and the precipitate of *p*-nitraniline hydrochloride filtered. The benzene filtrate, when concentrated under reduced pressure, deposited, first at a volume of 100 cc., 1.0 g. of *p*-nitraniline, then at a volume of 70 cc., 11 g. of *p*-nitrophenyl isothiocyanate, m. p. 112–113°. The mother liquor on further evaporation yielded a total of 10.8 g. of the same substance. The last precipitate from the concentrated mother liquor was contaminated with di-*p*-nitrophenylthiourea, from which the iso-

[19] Private communication from Professor Hesse.

[20] Coghill and Johnson, THIS JOURNAL, **47**, 187 (1925).

thiocyanate could be separated by extraction with cold benzene. Too long heating or local superheating of the reaction mixture increased the quantity of thiourea formed.

**Nitroaryl Thioureas.**—The thioureas were prepared by the addition of an aniline derivative to an isothiocyanate. The most successful methods of procedure are shown in Table IV and the properties of the thioureas are given in Table V.

TABLE IV

PREPARATION OF NITROARYLTHIOUREAS

| | Reactants | Cc. solvent | Time of boiling | Yield of thiourea, % | |
|---|---|---|---|---|---|
| 1 | 20 g. $p$-$NO_2C_6H_4NCS$<br>10.5 cc. $C_6H_5NH_2$ | 90 $C_6H_6$ | 3 min. | $p$-$C_6H_5NHCSNHC_6H_4NO_2$[21] | 97 |
| 2 | 5 g. $p$-$NO_2C_6H_4NCS$<br>3.8 g. $p$-$NO_2C_6H_4NH_2$ | 100 $C_6H_6$<br>2 $C_5H_5N$ as catalyst[22] | 1 hr. | $p$-$CS(NHC_6H_4NO_2)_2$ | 94 |
| 3 | 10 g. $C_6H_5CONCS$<br>8.5 g. $p$-$NO_2C_6H_4NH_2$ | 70 $C_6H_6$ | 15 min. | $p$-$C_6H_5CONHCSNHC_6H_4NO_2$ | 96 |
| 4 | 10 g. $C_6H_5CONCS$<br>8.5 g. $m$-$NO_2C_6H_4NH_2$ | 125 $C_6H_6$ | Stood in cold 2 hr. | $m$-$C_6H_5CONHCSNHC_6H_4NO_2$ | 96 |

TABLE V

PHYSICAL PROPERTIES OF NITROARYLTHIOUREAS

| | Thiourea | M. p., °C. | Crystalline form | Analyses, % Nitrogen Calcd. | Nitrogen Found | Sulfur Calcd. | Sulfur Found |
|---|---|---|---|---|---|---|---|
| 1 | $p$-$C_6H_5NHCSNHC_6H_4NO_2$ | 160 | Pale yellow plates from acetone | 15.38 | 15.22 | 11.71 | 11.81 |
| 2 | $p$-$CS(NHC_6H_4NO_2)_2$ | 195–196 | Orange needles[23] from acetone | 17.61 | 17.50 | 10.06 | 10.35 |
| 3 | $p$-$C_6H_5CONHCSNHC_6H_4NO_2$[24] | 182 | Pale yellow needles from acetic acid | 14.00 | 13.93 | 10.63 | 10.75 |
| 4 | $m$-$C_6H_5CONHCSNHC_6H_4NO_2$[24] | 164–165 | Pale yellow needles from acetic acid | 14.00 | 13.92 | 10.63 | 10.65 |

**S-Methylphenyl-$p$-nitrophenylpseudothiourea.**—Phenyl-$p$-nitrophenylthiourea was alkylated in 72% yield by treatment with methyl iodide in methanol solution. Ten grams of thiourea was suspended in 40 cc. of absolute methanol, 5.5 g. of methyl iodide was added and the mixture was boiled for half an hour. The resulting clear solution was iced and treated with 3 cc. of pyridine, when, on stirring, 6 g. of a precipitate of the free base, melting at 120–122°, was obtained. From the filtrate, by adding 200 cc. of cold water, 3.5 g. melting at 103–105° was precipitated. This mixture was resolved, by repeated fractional crystallization from absolute methanol, into 1.6 g. of the alkylated pseudothiourea, melting at 118–120°, and 0.3 g. of the original thiourea, melting at 160°. When recrystallized from absolute methanol, the alkylated product separated in the form of long yellow needles, melting at 121–122°.

*Anal.* Calcd. for $C_{14}H_{13}O_2N_3S$: N, 14.63; S, 11.15. Found: N, 14.62; S, 11.28.

**$\alpha$-$p$-Nitrophenyl-$\beta,\gamma$-diphenylguanidine.**—This guanidine was obtained (a) in 80%

[21] This thiourea could not be prepared by treating phenyl isothiocyanate with $p$-nitraniline, neither by fusion of the two substances, nor by heating a solution of the two in the presence of hydrochloric acid or pyridine as catalyst.

[22] No reaction took place unless catalyzed by pyridine.

[23] The thiourea separated from solutions in the form of curved yellow needles, which became orange on exposure to the air.

[24] Neither of these products is the same as a nitrophenylbenzoylthiourea prepared by Miquel by direction nitration; *Ann. chim. phys.*, [5] **11**, 322 (1877).

yield by treating *p*-nitrophenylphenylthiourea with aniline in the presence of pyridine and iodine, and (b) in 70% yield by fusing S-methyl-*p*-nitrophenylphenylpseudothiourea with aniline.

(a) Ten grams of *p*-nitrophenylphenylthiourea and 3.5 cc. of aniline were dissolved in 20 cc. of pyridine, a solution of 9.3 g. of iodine in 40 cc. of pyridine was added together with 20 cc. of pyridine for washing, and the mixture was heated to boiling. After one minute of boiling the starch test showed the absence of free iodine. When the reaction mixture was cooled and treated with 300 cc. of cold water, a gummy precipitate was obtained which became crystalline on standing for three hours in an ice-bath. The precipitate was filtered, dried and treated with 125 cc. of cold acetone. The acetone solution, when filtered from the undissolved sulfur and concentrated to a volume of 40 cc., yielded 7.3 g. of the guanidine, melting at 170–171°. By concentrating the filtrate and adding cold alcohol, an additional 2.3 g. of the guanidine was obtained. When purified by recrystallization from acetone, the guanidine separated in the form of yellow leaves, which melted at 172–173°. One gram dissolved in 12 cc. of boiling, and in 20 cc. of cold acetone. The guanidine was extremely resistant to hydrolysis. It was recovered unchanged after heating for several hours in contact with concentrated hydrochloric acid, 70% sulfuric acid, or 40% sodium hydroxide.

*Anal.* Calcd. for $C_{19}H_{16}O_2N_4$: C, 68.68; H, 4.82; N, 16.87. Found: C, 68.49; H, 4.85; N, 16.74.

It is to be noted that all attempts to prepare a mononitrotriphenylguanidine by treating diphenylthiourea with *p*-nitraniline, a reaction analogous to (a), were unsuccessful. When a pyridine solution containing 5 g. of diphenylthiourea and 3.0 g. of *p*-nitraniline was treated with iodine according to the procedure described above, the only products isolated from the reaction mixture were 0.3 g. of di-*p*-nitrophenylphenylguanidine, melting at 191–193°, and 0.3 g. of tri-*p*-nitrophenylguanidine, melting at 244–245°. The rest of the material was an oil. The use of basic lead carbonate or mercuric chloride as desulfurizing agent was likewise unsuccessful.

(b) Two grams of S-methyl-*p*-nitrophenylphenylpseudothiourea and 0.9 g. of aniline were heated at the fusion temperature for fifteen minutes. The melt was cooled, dissolved in alcohol, and the alcohol solution concentrated to a volume of 30 cc. On cooling, 1.1 g. of the guanidine, melting at 170–171°, was precipitated. The filtrate yielded 0.5 g. of the same product.

**β-Phenyl-α,γ-di-*p*-nitrophenylguanidine.**—This di-*p*-nitrophenylphenylguanidine was obtained (a) by the reaction between di-*p*-nitrophenylthiourea and aniline in the presence of iodine and pyridine, (b) by the isomerization of the higher-melting di-*p*-nitrophenylphenylguanidine, and (c) by the condensation of phenyl-isocyan-dichloride with *p*-nitraniline.

(a) Five grams of di-*p*-nitrophenylthiourea was suspended in 30 cc. of pyridine, and 1.9 cc. of aniline was added. When a solution of 4.0 g. of iodine in 20 cc. of pyridine was added, together with 15 cc. of pyridine for washing, an immediate exothermic reaction took place. The reaction was complete after boiling for one minute. The product was isolated by a procedure analogous to that described above for the preparation of *p*-nitrophenyldiphenylguanidine. By treatment with ice water, acetone and alcohol, 5 g. of the guanidine was obtained which melted at 166–168°. The alcohol filtrate yielded 0.5 g., melting at 165–192°, which consisted of a mixture of the guanidine melting at 168–169°, and the isomeric form melting at 191–193°.

The guanidine, when recrystallized from alcohol, separated in the form of yellow prismatic needles containing one mole of alcohol of crystallization. One gram dissolved in 48 cc. of hot, and in 400 cc. of cold alcohol. When alcohol-free after heating at 120°, the substance melted at 168–169°.

*Anal.* Calcd. for $C_{19}H_{15}O_4N_4$: C, 60.43; H, 4.09; N, 18.57. Found: C, 60.77; H, 3.85; N, 18.65.

(b) The guanidine melting at 168–169° was also obtained by the action of hydrogen chloride upon the isomeric guanidine melting at 191–193°. Five-tenths of a gram of the latter was suspended in 100 cc. of concd. hydrochloric acid, and the mixture was heated on the steam-bath for eight hours. The mixture was then neutralized with ammonia, the precipitate taken up in hot alcohol and treated again with ammonia. On cooling the solution, 0.3 g. of the guanidine, melting at 165–167°, was obtained. The filtrate yielded 0.1 g. of the original higher melting form.

(c) Inasmuch as the yield of guanidine from condensation of phenyl-isocyandichloride with *p*-nitraniline was only 40% of the theoretical, the details of this procedure will be omitted.

**α,β-Di-*p*-nitrophenyl-γ-phenylguanidine.**—The di-*p*-nitrophenylphenylguanidine melting at 191–193° was prepared: (a) by treating *p*-nitrophenylphenylthiourea with *p*-nitraniline in the presence of iodine and pyridine, (b) by isomerization of the di-*p*-nitrophenylphenylguanidine melting at 168–169°, and (c) by fusing S-methyl-*p*-nitrophenylphenylpseudothiourea with *p*-nitraniline.

(a) Ten grams of *p*-nitrophenylphenylthiourea and 5.1 g. of *p*-nitraniline were suspended in 30 cc. of pyridine, a solution of 9.3 g. of iodine in 35 cc. of pyridine was added, and the mixture was boiled for five minutes. On cooling the resulting solution and adding 400 cc. of water, a gum was obtained. When the aqueous pyridine solution was decanted and the gum stirred with 50 cc. of alcohol, a crystalline precipitate (A) was obtained which weighed 5 g. and melted at 220–238°. The filtrate, when evaporated to a gum and stirred with 50 cc. of alcohol, yielded a second crop (B) of crystalline precipitate, which weighed 5.2 g. and melted partially with the evolution of a gas at 90°, solidified at 115°, and melted to a clear oil at 190–280°.

Precipitate (A), when extracted three times with 30-cc. portions of boiling acetone yielded, by evaporation of the extracts, 4.0 g. of tri-*p*-nitrophenylguanidine.

Precipitate (B) was treated with 50 cc. of cold acetone, filtered from sulfur, and the filtrate concentrated to a volume of 10 cc. When 15 cc. of alcohol was added, 4.3 g. of the di-*p*-nitrophenylphenylguanidine crystallized from the cold solution. The filtrate yielded 0.5 g. of the same product. The guanidine was recrystallized from alcohol, from which it separated in the form of yellow prisms, which held one mole of alcohol of crystallization. One gram dissolved in 40 cc. of boiling, and in 200 cc. of cold alcohol. The pure guanidine, when heated in a melting point tube, melted partially with the evolution of alcohol of crystallization at 90–105°, solidified at 120°, and melted sharply at 191–193°. When alcohol-free, the substance melted at 191–193°.

*Anal.* Calcd. for $C_{19}H_{15}O_4N_5$: C, 60.43; H, 4.09; N, 18.57. Found: C, 60.09; H, 4.02; N, 18.39. Calcd. for $C_{19}H_{15}O_4N_5 \cdot C_2H_6O$: N, 16.55. Found: N, 16.45.

The products of the reaction between *p*-nitraniline and *p*-nitrophenylphenylthiourea in the presence of pyridine and iodine are, therefore, the di-*p*-nitrophenylphenylguanidine, melting at 191–193°, obtained in 34% yield, and the tri-*p*-nitrophenylguanidine, obtained in 30% yield. Evidence as to the mechanism of the formation of the latter was secured from a reaction carried out in chloroform solution. Under these conditions di-*p*-nitrophenylthiourea was isolated from the reaction mixture in addition to the above products. The occurrence of this substance indicates that it is a possible precursor of the tri-*p*-nitrophenylguanidine formed.

(b) The higher melting di-*p*-nitrophenylphenylguanidine was also obtained by isomerization of the lower melting form by heat or pyridine.

The guanidine melting at 168–169° was transformed quantitatively into the guanidine melting at 191–193° when 0.5-g. specimens of the former were heated for thirty

minutes at 170–175°. Partial isomerization was brought about by heating at lower temperatures (130–170°), when mixtures melting from 164 to 193° were obtained.

The guanidine melting at 168–169° was partially converted into the higher melting guanidine by heating in pyridine solution. When a pyridine solution of 4 g. of the former substance was boiled for one hour, a mixture of the two isomers was obtained which was separated by repeated fractional extractions with acetone and alcohol into 2.2 g. of the guanidine melting at 191–193°, and 1.4 g. of the guanidine melting at 168–169°.

(c) The guanidine melting at 191–193° was obtained in 26% yield by fusing S-methyl-*p*-nitrophenylphenylpseudothiourea with *p*-nitraniline.

**β-Phenyl-α,γ-di-*m*-nitrophenylguanidine.**—This guanidine was prepared in 65% yield by treating phenyl-isocyan-dichloride with *m*-nitraniline. A solution containing 8 g. of phenyl-isocyan-dichloride and 14 g. of *m*-nitraniline in 80 cc. of dry chloroform was boiled for three hours. The hydrochloride obtained on cooling and filtering the reaction mixture was changed into 5.8 g. of the free guanidine by treating its alcohol solution with ammonia. By continued boiling of the mother liquor from the reaction with fresh *m*-nitraniline, an additional 5.6 g. of the guanidine was obtained.

When recrystallized from alcohol, the guanidine separated in the form of yellow plates, melting at 175–176°. One gram of the substance was soluble in 50 cc. of boiling alcohol and in 75 cc. of cold alcohol.

*Anal.* Calcd. for $C_{19}H_{15}O_4N$: C, 60.43; N, 18.57. Found: C, 60.61; N, 18.69.

**α,β,γ-Tri-*p*-nitrophenylguanidine.**—The most successful method of preparing tri-*p*-nitrophenylguanidine consisted in desulfurizing a mixture of di-*p*-nitrophenylthiourea and *p*-nitraniline by means of iodine and pyridine. Other desulfurizing agents, such as lead hydroxide, led to the formation of the oxygen urea, di-*p*-nitrophenylurea.

Fifteen grams of di-*p*-nitrophenylthiourea and 6.6 g. of *p*-nitraniline were dissolved in 90 cc. of hot pyridine, a solution of 12 g. of iodine in 40 cc. of pyridine was added, and the mixture was boiled for four hours. It was then cooled, and the product precipitated by adding water gradually with stirring. The yellow precipitate was filtered, washed with water to remove pyridine hydriodide and with carbon bisulfide to remove sulfur. The product was purified by extracting it three times with 100 cc. of acetone, and once with 50 cc. of acetone. The extracts, when concentrated, deposited a total of 14.6 g. of the guanidine, melting at 241–243°. The yield was 73%. The residue insoluble in acetone consisted of 0.9 g. of di-*p*-nitrophenylurea, melting with decomposition at 310°.

The guanidine was purified by recrystallization from acetone. Twelve grams dissolved in 320 cc. of boiling acetone, and the solution, when concentrated to 50 cc., deposited 8.8 g. of transparent yellow plates, melting at 244–245°. The guanidine was very slightly soluble in alcohol or chloroform.

*Anal.* Calcd. for $C_{19}H_{14}O_6N_6$: C, 54.02; H, 3.32; N, 19.90. Found: C, 53.82; H, 3.42; N, 19.79.

**α-*p*-Aminophenyl-β,γ-diphenylguanidine.**—Four grams of α-*p*-nitrophenyl-β,γ-diphenylguanidine was dissolved in 95 cc. of hot ethyl acetate, 0.42 g. of platinum oxide catalyst[25] was added, and the mixture was shaken in an atmosphere of hydrogen under twenty pounds pressure. After a slow absorption of hydrogen during the first hour, 0.15 g. of fresh catalyst was added, and the shaking was continued for three hours. At the end of this time a sample of the solution, filtered from platinum, gave a red coloration with sodium hydroxide. Since this test is characteristic of the nitro com-

[25] Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

pound, 0.15 g. of fresh catalyst was added, the mixture was shaken for five hours longer, and then allowed to stand without shaking for twelve hours under twenty pounds pressure. After this treatment the solution gave no coloration with alkali. The catalyst was then filtered off, and the solution concentrated under reduced pressure at 60° to a gum. The gum was dissolved in absolute alcohol, the alcohol distilled off, and the process repeated until a crystalline precipitate separated from the concentrated alcohol solution. This consisted of 2.3 g. of the amino compound, melting at 152–153°. An additional 0.2 g. of the same product was obtained from the filtrate, which gave a total yield of amino compound amounting to 69%.

The guanidine derivative, when recrystallized from absolute alcohol, separated in the form of short, colorless needles, melting at 152–153°. One gram dissolved in 25 cc. of boiling alcohol and in 30 cc. of cold alcohol. The substance was slightly soluble in water, giving a basic solution.

*Anal.* Calcd. for $C_{19}H_{18}N_4$: N, 18.54. Found: N, 18.53, 18.33.

**β-Phenyl-α,γ-di-*p*-aminophenylguanidine.**—This amino compound was obtained by reduction of either the nitro compound melting at 168–169°, or the nitro compound melting at 191–193°.

Ten grams of the nitro compound, melting at 168–169°, was dissolved in 100 cc. of hot purified ethyl acetate and shaken with 0.2 g. of platinum oxide in an atmosphere of hydrogen for fifty-five minutes. The solution was then filtered from the platinum, and concentrated under reduced pressure to a volume of 40 cc. At this point a yellowish precipitate separated, which consisted of 3.9 g. of the amino compound, melting at 166–167°. By evaporation of the filtrate, 3.7 g. more of the same product was obtained (a 78% yield).

When decolorized with norite and recrystallized from alcohol, the substance separated in the form of rosets of colorless plates, m. p. 167–168°. A mixture of the amino derivative with the original nitro compound melted at 120–130°. The amino compound was moderately soluble in water, giving a strongly basic solution. Solutions of the amino compound discolored when allowed to stand in the air.

*Anal.* Calcd. for $C_{19}H_{19}N_5$: N, 22.08. Found: N, 21.98, 21.94.

The same amino compound was obtained in 61% yield by reduction of the nitro compound melting at 191–193°. The two specimens were identical in mixed melting point, crystalline form, and percentage of nitrogen.

**β-Phenyl-α,γ-di-*m*-aminophenylguanidine.**—This *m*-amino derivative was obtained in 80–90% yields by reduction of the *m*-nitro compound, m. p. 175–176°, according to a procedure similar to that described for the preparation of the *p*-amino compound. When purified by recrystallization from alcohol, the substance was obtained as a white powder, melting at 138–139°. It was moderately soluble in hot water, giving a strongly basic solution, but separated as an oil on cooling. One gram dissolved in 10 cc. of boiling alcohol and in 30 cc. of cold alcohol.

*Anal.* Calcd. for $C_{19}H_{19}N_5$: N, 22.08. Found: N, 22.09, 21.91.

**α,β,γ-Tri-*p*-aminophenylguanidine.**—Three grams of tri-*p*-nitrophenylguanidine suspended in 100 cc. of hot ethyl alcohol was shaken with 0.3 g. of platinum oxide under 23 pounds pressure of hydrogen. A rapid absorption of hydrogen occurred at once with the evolution of heat. As the nitro compound dissolved, a white amino compound was precipitated on the walls of the flask. The reaction was complete in less than an hour. The resulting mixture was poured into a beaker, treated with 12 cc. of water, and heated to boiling to dissolve the amino compound. The platinum was filtered off, and the solution concentrated at once under reduced pressure to a volume of 40 cc. On cooling, the solution deposited a gray precipitate of 0.9 g., melting at 211°, and

from the filtrate 1.1 g. of the same substance was obtained. The residue was a black gum.

The product, when treated with norite and crystallized from 80% aqueous alcohol, melted at 215°. Two grams dissolved in 100 cc. of 80% aqueous alcohol and, on cooling the solution, 0.7 g. separated in the form of long, colorless needles. One gram was soluble in 400 cc. of boiling acetone and did not crystallize on cooling. The substance was only slightly soluble in pure alcohol or water. Solutions of the compound quickly turned purple when exposed to the air. This triamino compound was by far the least soluble and the most sensitive to decomposition of any of the amino derivatives studied.

*Anal.* Calcd. for $C_{19}H_{20}N_6$: N, 25.30. Found: N, 25.10, 25.08.

## Summary

1. A new method for the synthesis of nitrotriarylguanidines has been developed. By desulfurization of a mixture of the thiourea and amine through the combined action of iodine and pyridine, *p*-nitrophenyldiphenylguanidine, two di-*p*-nitrophenylphenylguanidines, and tri-*p*-nitrophenylguanidine have been prepared. A di-*m*-nitrophenylphenylguanidine has also been obtained.

2. An instance of guanidine isomerism has been observed in the case of the two di-*p*-nitrophenylphenylguanidines. These substances are interconvertible isomers, which differ widely in melting points and in behavior toward heat, acids and pyridine.

3. Four previously undescribed nitroarylthioureas have been prepared.

4. Four amino derivatives of triphenylguanidine have been obtained, and their pharmacological effect on the tubercle bacillus has been investigated.

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

# IODINATION IN LIQUID AMMONIA

BY THOMAS H. VAUGHN AND J. A. NIEUWLAND

RECEIVED SEPTEMBER 29, 1931 PUBLISHED FEBRUARY 5, 1932

Solutions of iodine in liquid ammonia have been used by several investigators as a nitridizing agent.[1] In these reactions hydrogen has been nitridized off of organic compounds with the subsequent formation of ammonium iodide. A survey of the literature shows that no substitutions of iodine for hydrogen have been reported.

It has been pointed out by Richter[2] and shown by Datta and Chatterjee[3] that iodination generally takes place most readily in the presence of sub-

[1] Shurman and Fernelius, THIS JOURNAL, **52**, 2425–30 (1930); Strain, *ibid.*, **51**, 272 (1929); **49**, 1564 (1927); Bergstrom, *J. Phys. Chem.*, **32**, 440 (1928).

[2] Richter, "Organic Chemistry," translation by Spielmann, Blakiston's Son & Co., Philadelphia, 1919, Vol. I, p. 92.

[3] Datta and Chatterjee, THIS JOURNAL, **39**, 439 (1917).

stances which combine with the hydrogen iodide produced. From this consideration liquid ammonia would appear to be a suitable medium in which to carry out iodinations since any hydrogen iodide produced would at once react with the ammonia to produce ammonium iodide.

Such has proved to be the case. Iodine in liquid ammonia is capable of replacing various types of labile hydrogen. Substitution occurs in acetylenes, in ketones, in amines, and in compounds containing the —$COCH_2CO$— group. The reaction of iodine and acetylene in liquid ammonia affords a convenient method for the preparation of diiodoacetylene.

**Preparation of Diiodoacetylene.**—One hundred grams of iodine is placed in a 1.5-liter beaker and the bottom of the beaker cooled by immersion in a shallow dish of liquid ammonia. After standing for a minute or so, 750 ml. of ammonia is added as rapidly as possible.[4] Acetylene, from a Prestolite cylinder, washed with water and dried by spraying through concentrated sulfuric acid, is bubbled through the solution at a rate of 200 to 500 ml. per minute. The contents of the beaker should be mechanically stirred. In two and one-half to three hours the solution becomes perfectly clear, indicating the end of the reaction. The beaker is covered with a watch glass and placed in a hot water-bath to evaporate the ammonia. When the volume has been reduced to about 150 ml., 500 ml. of water is slowly added to precipitate the diiodoacetylene. The precipitate is filtered by suction and pressed as dry as possible by means of a sheet of rubber. The product should weigh 60–65 g. The moist diiodoacetylene is dissolved in 300 ml. of petroleum ether and treated with 35 g. of calcium chloride. After standing overnight, the solution is decanted from the calcium chloride into a tall beaker which is immersed in liquid ammonia. The diiodoacetylene which crystallizes is filtered off on a cold funnel.[5] A yield of 30–35 g. (54–63% of the theoretical) of material melting at 78.5–78.9° is obtained. By evaporating the mother liquor and cooling, a further 3–5 g. may be obtained. The moist material may also be dried by desiccation *in vacuo* under sulfuric acid, whereby 50–54 g. (90–97%) of diiodoacetylene can be obtained. This method of drying is not to be recommended, however, as partial decomposition occurs.

**Proof of Identity of Diiodoacetylene.**—Since diiodoethylene might also be formed by the action of iodine on acetylene, it was felt necessary to prove that the compound obtained was actually diiodoacetylene. An analysis would be of little value as the difference between the two compounds amounts to but two hydrogen atoms in a total molecular weight of 280. The melting point could not be used to identify the compound since values for this constant of the ethylenic and acetylenic compounds have been variously reported from 73–76° and 74–82°, respectively.

To prove its structure a portion of the substance was chlorinated by the procedure of Howell and Noyes.[6] A good yield of hexachloroethane, m. p. 185°, was obtained and no hydrogen chloride was produced. This proves the absence of hydrogen in the original compound.

To 15 g. of the compound in 100 ml. of benzene, 13.7 g. of iodine was added and the

[4] Ammonia has been added in this manner to as much as 200 g. of iodine a number of times without the occurrence of a single explosion. Although a violent reaction takes place and a small amount of iodine vapor is lost, the procedure appears to be perfectly safe.

[5] A convenient cold funnel can be made by inserting a 15-cm. funnel into a 25-cm. funnel, closing the annular opening by rubber tubing, and filling the space between the two funnels with liquid ammonia.

[6] Howell and Noyes, THIS JOURNAL, **42**, 991–1010 (1920).

mixture refluxed for one hour. The solution was allowed to stand overnight and deposited a crop of lemon yellow crystals of tetraiodoethylene, m. p. 188–9°.

Diiodoacetylene was prepared by the method of Dehn[7] and was found to melt at 78°. The melting point of a mixture of this material and that from the liquid ammonia synthesis was also 78°. The substance also gave a brown precipitate with ammoniacal cuprous chloride solution. Thus it is clearly shown that the substance obtained was actually diiodoacetylene.

To elucidate the mechanism of the reactions occurring in the iodination of acetylene, weighed samples of 0.5 to 1.0 g. of iodine were dissolved in ammonia and treated with acetylene. After completion of the reaction and evaporation of the ammonia, the amount of iodide ion produced was determined by titration with standard silver nitrate solution by the method of Fajans. It was found that exactly 50% of the iodine used was converted to iodide. Since the remaining 50% of iodine was obtained in the form of diiodoacetylene, the reaction may be represented by

$$C_2H_2 + 2I_2 + 2NH_3 \longrightarrow C_2I_2 + 2NH_4I$$

**Iodination of Sodium Acetylide.**—An attempt was made to prepare monoiodoacetylene by treating 1 mole of sodium acetylide in liquid ammonia with 1 mole of iodine. On adding water to the reaction mixture approximately 50% of the acetylene present as acetylide was liberated and a precipitate of diiodoacetylene was obtained. This is in accord with the work of Moissan,[8] who obtained tetraiodoethylene by the action of iodine on sodium acetylide in benzene and at variance with that of Skosarewski,[9] who reported the formation of triiodoethylene under similar circumstances. Since the reaction between iodine and sodium acetylide in ammonia is almost instantaneous it is recommended for the rapid preparation of diiodoacetylene.

**Decomposition of Diiodoacetylene.**—There are several references in the literature to the decomposition of diiodoacetylene. According to Baeyer,[10] on heating at 100° for some time, the compound explodes. Nef[11] states that violent explosions are caused by heating the substance in sealed or open tubes at 81–100° for two to twenty minutes. The products of these violent reactions are carbon and iodine. Meyer and Pemsel[12] and Schenk and Litzendorff[13] have shown that the decomposition can be controlled in solution to give tetraiodoethylene and carbon.

Since the material was at hand, the decomposition points of samples of eighteen different preparations of diiodoacetylene were measured. The decomposition point was determined by placing a small amount of the substance in a capillary tube, attaching to a thermometer, and heating in a Thiele melting point apparatus. As the decomposition point was reached the substance exploded with a sharp report and iodine vapor filled the tube. Of the eighteen preparations (two samples of each) the average decomposition point was 125°, the lowest being 121° and the highest 128°. On one occasion, however, a few grams in a test-tube exploded at 84°. At another time, during an attempted distillation *in vacuo*, 15 g. of the substance exploded at 98° and 4 mm. of pressure with sufficient violence to wreck the apparatus.

It has also been found that the substance can be set off by friction. Small amounts were placed in a mortar and struck a sharp blow with a pestle. An explosion of considerable violence, resembling that of nitrogen iodide in nature, took place in all cases.

[7] Dehn, THIS JOURNAL, **33**, 1598–1601 (1911).

[8] Moissan, *Compt. rend.*, **127**, 914 (1898).

[9] Skosarewski, *J. Russ. Phys.-Chem. Soc.*, 863–872 (1904).

[10] Baeyer, *Ber.*, **18**, 2275 (1885).

[11] Nef, *Ann.*, **298**, 347 (1897).

[12] Meyer and Pemsel, *Ber.*, **29**, 1411–1412 (1896).

[13] Schenk and Litzendorff, *ibid.*, **37**, 3453–3464 (1904).

### Miscellaneous Iodinations

**Ketones.**—When acetone was added to a solution of iodine in ammonia a slow reaction took place. After the disappearance of the color the solution was evaporated and water added, which precipitated 8 to 12% yields of iodoform, m. p. 119°. The precipitate was filtered off and the iodide content of the filtrate determined by the method of Fajans. Values of 87 to 90% of the iodine used were obtained.

Since it has been shown by Étard[14] that tribromoacetone is decomposed by ammonium hydroxide to give bromoform and ammonium acetate, it seems likely that the reactions which occur are as follows

$$CH_3—CO—CH_3 + 3I_2 + 3\ NH_3 \longrightarrow CCl_3—CO—CH_3 + 3NH_4I$$
$$CI_3—CO—CH_3 + NH_4OH \longrightarrow HCI_3 + CH_3—CO—ONH_4$$

These equations, however, fail to account for the large amount of iodide ion which is found in the filtrate.

Dawson and Leslie[15] have shown that in aqueous and non-aqueous solutions the rate of reaction of iodine with acetone is proportional to the hydrogen-ion concentration. In liquid ammonia the ammonium ion plays the same role as the hydrogen ion does in water. Reaction mixtures of iodine and acetone in ammonia to which ammonium nitrate had been added were found to clear up much more rapidly than similar uncatalyzed mixtures. No exact measurements of rate were made.

Methyl ethyl ketone also reacts with iodine in ammonia giving 92 to 96% of iodide and 2 to 5% of iodoform.

**Amines.**—Mono- and dibutylamines react slowly with iodine in ammonia. On treatment with water, heavy, red, insoluble oils were obtained which could not be crystallized and which on heating decomposed with the evolution of iodine vapor. No definite compounds were isolated.

**Compounds of the Structure** —CO—$CH_2$—CO—.—Malonic ester reacts with iodine in ammonia almost instantaneously and gives a red, viscous oil which is insoluble in water, and which decomposes on heating with the liberation of iodine vapor. Acetoacetic ester also immediately decolorizes ammonia solutions of iodine. The products of this reaction were not investigated.

**No Reaction.**—Benzene, ethylene, trimethylethylene, propylene, pentane and triphenylmethane did not react with iodine in ammonia at the boiling point of the solution at atmospheric pressure.

## Conclusions

1. Liquid ammonia has been found to be an excellent medium in which to carry out certain iodinations.

2. Iodine in ammonia reacts with acetylene and with sodium acetylide to give diiodoacetylene in good yield. A method of preparation has been based on this reaction.

3. The decomposition point of diiodoacetylene has been determined and found to be 125 ± 4°. It has also been found that diiodoacetylene can be detonated by a sharp blow.

4. Acetone reacts with iodine in ammonia and gives 8 to 12% yields of iodoform. Methyl ethyl ketone also reacts, giving smaller yields of the same material.

[14] Étard, *Compt. rend.*, **114**, 754 (1892).

[15] Dawson and Leslie, *J. Chem. Soc.*, **95**, 1863 (1909).

5. Mono- and dibutylamines, malonic ester, and acetoacetic ester react with ammonia solutions of iodine. No definite compounds were isolated from the reaction products.

6. Benzene, ethylene, trimethylethylene, propylene, pentane, and triphenylmethane do not react with iodine under the conditions studied.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PEIPING UNION MEDICAL COLLEGE, PEIPING]

# EFFECT OF ULTRASONIC RADIATION ON INDICATORS

BY SZU-CHIH LIU AND HSIEN WU

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In a study on oxidations promoted by ultrasonic radiation, Schmitt, Johnson and Olson[1] found that when a dilute aqueous solution of brom thymol blue (to which sufficient sodium hydroxide was added to produce a blue-green color) was radiated, the solution became yellow in a very short time. Since the addition of alkali caused a prompt return of the blue color they concluded that comparatively few of the dye molecules were destroyed but they were "altered by the radiation and give rise to hydrogen ions." This seems to us a very significant finding, and we have repeated and extended their experiments. Unfortunately our results do not confirm theirs.

## Experimental

The oscillating current was generated by two 75-watt tubes (UX852) connected in a modified Hartley circuit. The quartz plate (about 47 × 50 mm.) lay between two brass electrodes, the distance between which could be adjusted. The vibrating part was placed in a dielectric liquid, xylene or benzene. The quartz plate vibrated at the rate of $1.3 \times 10^6$ times per second. On the upper electrode was placed a cooling coil of glass tubing through which cold water circulated.

Indicators used in this investigation were: thymol blue, brom phenol blue, brom cresol green, chlor phenol red, brom cresol purple, brom thymol blue, phenol red, congo red, methyl red, litmus, alizarin red and methyl violet.

About 15 cc. of dilute aqueous solution of each indicator (3 drops of 0.04% indicator solution in 15 cc.) was placed in a small, thin test-tube 15 mm. in diameter. The tube was held so that its bottom was just buried in the mount of the vibrating dielectric. After exposing for ten minutes, the tube was taken out and its color compared with that of the unexposed control. The temperature of the indicator solutions never rose above 35°.

[1] Schmitt, Johnson and Olson, THIS JOURNAL, **51**, 370 (1929).

**1. Unbuffered Solutions.**—Unbuffered solution of each indicator was adjusted to show an alkaline reaction such that the addition of one drop of $N/10$ hydrochloric acid would cause it to show an acid reaction, or a distinct change of color. After an exposure of ten minutes, the color of all indicator solutions became lighter than the unexposed control. Some of them even turned colorless but none showed acid color. The exposed solution of each indicator was, then, divided into two equal portions. To one portion were added two drops of $N/10$ sodium hydroxide and the resulting color compared with the other portion as control. It was found that addition of sodium hydroxide did not cause a return of the original color. If the change in color were due to hydrogen ions formed by ultrasonic radiation, two drops of $N/10$ sodium hydroxide would certainly be enough to neutralize them. The control portion of each radiated solution was left to stand overnight, and none of them showed a return of the original color. This observation shows that the indicator molecules are permanently destroyed by radiation.

**2. Buffered Solutions.**—The indicator solutions were buffered to show an alkaline reaction. They were radiated for ten minutes, and the color faded just as in the case of the unbuffered solutions. This shows that color fading is not due to the change of $P_H$ of the indicator solution.

**3. Gas-free Unbuffered Solutions.**—Vigorous cavitation of the dissolved air from the radiated solution suggests that oxidation might be the cause of the destruction of indicator molecules, since Schmitt, Johnson and Olson have obtained positive tests for the presence of hydrogen peroxide in the radiated solution. To test this hypothesis the indicator solutions were made gas-free before radiation. This was done by boiling the indicator solutions for five minutes in small test-tubes and then a layer of liquid paraffin was laid on the surface. The gas-free solutions, when radiated, showed no change of color.

**4. Unbuffered Solutions Saturated with Oxygen or Hydrogen.**—Indicator solutions made gas-free by boiling were saturated with oxygen or hydrogen after cooling. With oxygen, color faded very rapidly when the solution was radiated and the addition of two drops of $N/10$ sodium hydroxide did not cause a return of the original color, but no fading of color was observed in solutions saturated with hydrogen.

The above observations show conclusively that the indicators are permanently destroyed under the influence of ultrasonic radiation. A change of hydrogen-ion concentration may occur as a result of this destruction, but the fading of the color is due to the destruction of the indicator and not to any change in hydrogen-ion concentration. Since only solutions containing air or oxygen show color fading, the destruction of the indicator must be due to oxidation. It would seem that the traces of hydrogen peroxide which Schmitt, Johnson and Olson have detected might be

responsible for the oxidation, but we have added large amounts (1 cc. of 2% solution) of hydrogen peroxide to 15 cc. of the dilute indicator solution without observable effect. It is probable that the dissolved oxygen is directly activated by ultrasonic radiation.

## Summary

Twelve unbuffered indicator solutions, saturated with air or oxygen, showed color fading when exposed to ultrasonic radiation. Buffered solutions gave the same result. The color of gas-free solutions and solutions saturated with hydrogen did not fade when exposed. These observations show that indicator molecules are permanently destroyed by oxidation under the influence of ultrasonic radiation.

PEIPING, CHINA

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[CONTRIBUTION NO. 81 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

# DESOXYCODEINE STUDIES. III. THE CONSTITUTION OF THE SO-CALLED α-DIHYDRODESOXYCODEINE: BIS-DIHYDRODESOXYCODEINE[1]

BY ERICH MOSETTIG, FRANK L. COHEN AND LYNDON F. SMALL

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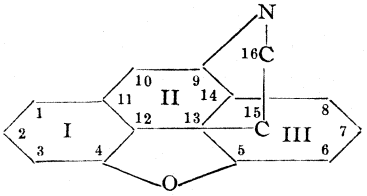
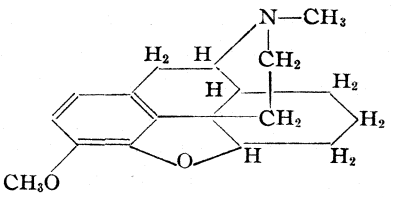
In the second paper of this series[2] five isomeric dihydrodesoxycodeines were described, of which four are phenolic in nature, and the fifth (dihydrodesoxycodeine-D) still contains the codeine cyclic ether structure intact (formula II).




I. Numbering system




II. Dihydrodesoxycodeine-D

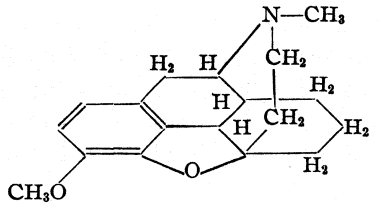
Dihydrodesoxycodeine-D represents the only possible non-phenolic member of this class, provided no isomerism appears as a result of steric differences at the asymmetric carbon atoms 5, 9, 13 or 14. Nowhere in morphine chemistry is there any convincing evidence which warrants the expectation of such a stereoisomerism.[3]

[1] This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

[2] Small and Cohen, THIS JOURNAL, 53, 2227 (1931).

[3] Ref. 2, pp. 2231, 2232.

Freund and his co-workers[4] described in 1921 an amorphous alkali-insoluble base which was obtained by reduction of α-chlorocodide in the presence of colloidal palladium. This substance analyzed approximately for $C_{18}H_{23}O_2N + {}^1/_2H_2O$, and although no evidence was advanced to show that the base was homogeneous, it was classified as a dihydrodesoxycodeine (designated α-) to which Freund assigned the formula III. This is identical with the structural formula which represents dihydrodesoxycodeine-D. In view of this apparent contradiction, the present investigation of the so-called α-dihydrodesoxycodeine was undertaken. Freund's experiment was repeated by Mannich,[6] who confirmed the formation of the amorphous base, and noted traces of crystalline compounds, identical with those obtained by similar reduction of β-chlorocodide.




III. α-Dihydrodesoxycodeine (Freund)[5]

When α-chlorocodide is hydrogenated in acetic acid solution in the presence of colloidal palladium according to Freund's directions,[7] a 95% yield of a well-crystallized base of m. p. 107° is obtained. This compound is identical with dihydrodesoxycodeine-D. The reduction proceeds slowly (Experiment 9).

With palladium on barium sulfate as catalyst, the result of the reduction is substantially the same, in that dihydrodesoxycodeine-D is formed in quantitative yield. In this experiment also the reduction ran slowly (Experiments 1 and 2). When, however, the amount of catalyst is increased (Experiment 3), the speed of reduction is also increased, and dihydrodesoxycodeine-D is formed only to the extent of about 40%. As other products were found 5% of tetrahydrodesoxycodeine and a 45% yield of an alkali-insoluble amorphous compound which represents the amorphous base described by Freund and Mannich.

When the hydrogenation was carried out with a palladium–calcium carbonate catalyst, the amorphous base was formed to the extent of 95–100%. Crystalline products could be isolated only in traces (Experiments 4 and 5). With platinum oxide as the catalyst, the amorphous base was obtained exclusively (Experiments 6, 7 and 8).

Regarding the catalytic hydrogenation of β-chlorocodide, a stereoisomer

[4] Freund, Melber and Schlesinger, *J. prakt. Chem.*, **101**, 1 (1921).

[5] In accordance with the at that time accepted Knorr–Hörlein structure for the morphine series, Freund linked C-15 to C-5. The uncertainty in regard to the morphine structure at this linkage has no bearing upon the isomerism in question.

[6] Mannich and Löwenheim, *Arch. Pharm.*, **258**, 300 (1920).

[7] An exact reproduction of Freund's experiment was impossible because of the lack of details given regarding volume of solvent, amount of catalyst and time required for the reduction.

of α-chlorocodide, contradictory statements have appeared in the literature. By reduction in the presence of palladium on charcoal, Mannich obtained as the main product the base which we have named dihydrodesoxycodeine-D, together with small amounts of a second base which Kondo[8] and Small[9] have shown to be tetrahydrodesoxycodeine. Speyer and Krauss,[10] on the other hand, reduced β-chlorocodide (at that time believed to be allopseudochlorocodide) using colloidal palladium and obtained what was claimed to be the so-called α-tetrahydrodesoxycodeine (dihydrodesoxycodeine-A).

The reduction of β-chlorocodide with palladium–barium sulfate, which gives substantially the results obtained by Mannich, is described in paper II of this series.[2] When colloidal palladium is used (Experiment 10) or palladium on calcium carbonate (Experiment 11), the product likewise consists of about 70% dihydrodesoxycodeine-D and 30% tetrahydrodesoxycodeine. With platinum oxide, the reduction runs very rapidly to completion, and results in a quantitative yield of tetrahydrodesoxycodeine, with absorption of three moles of hydrogen (Experiments 12 and 13). The isomers α- and β-chlorocodide behave alike in that both are reduced in the presence of the less active catalysts to dihydrodesoxycodeine-D. They differ under the influence of the more active catalysts; α-chlorocodide gives the amorphous base as end-product, while β-chlorocodide goes to tetrahydrodesoxycodeine with absorption of three moles of hydrogen.

Bromocodide behaves like α-chlorocodide toward catalytic reduction. In the presence of palladium–barium sulfate, it gives a 94% yield of dihydrodesoxycodeine-D (Experiment 14), whereas with palladium–calcium carbonate or platinum oxide yields of 93 and 100%, respectively, of the amorphous base were obtained (Experiments 15 and 16). From evidence in the thiocodide series Pschorr[11] concluded that the one known bromocodide must have the same configuration as β-chlorocodide. This question is still not definitely settled. The unexpected similar behavior of α-chlorocodide and bromocodide in our reduction experiments is not necessarily an argument against the above hypothesis.

The one known iodocodide[12] likewise gives the same catalytic reduction products as α-chlorocodide. With a palladium–barium sulfate catalyst 70% dihydrodesoxycodeine-D and 25% amorphous base are obtained.

**The Amorphous So-called α-Dihydrodesoxycodeine.**—The separation of the reduction products described above was accomplished most expeditiously by sublimation in high vacuum. At the temperature em-

[8] Kondo and Ochiai, *Ber.*, **63**, 646 (1930); Ochiai, *J. Pharm. Soc. Japan*, **568**, 91 June (1929).

[9] See following paper, Small and Cohen, THIS JOURNAL, **54**, 802 (1932).

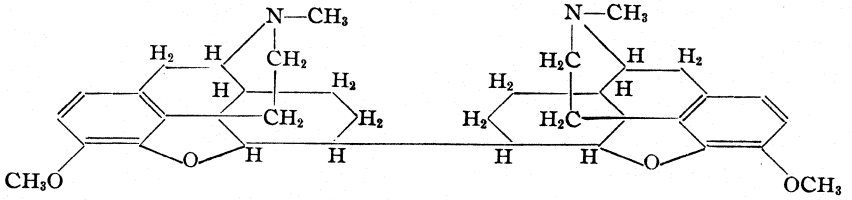
[10] Speyer and Krauss, *Ann.*, **432**, 233 (1923).

[11] Pschorr and Rollett, *ibid.*, **373**, 1 (1910); *cf.* Faltis, *Arch. Pharm.*, **255**, 85 (1917).

[12] *Cf.* Small and Cohen, THIS JOURNAL, **53**, 2216, 2222 (1931).

ployed the amorphous base was undecomposed, and not at all volatile; the sublimate could be separated by the use of tartaric acid, as described in paper II. The amorphous base which we obtain is obviously the same as that of Freund and Mannich. It seems probable, however, that Freund never obtained the base free from the small amounts of accompanying crystalline compounds (see below).

The amorphous base yielded no crystalline salts. Its very high boiling point, in comparison with the easily distillable hydrogenated desoxycodeines, indicated that it could scarcely be a simple dihydrodesoxycodeine. It proved in fact to be a dimolecular compound, which was probably formed in a manner analogous to the formation of diphenyl by catalytic dehalogenation of bromobenzene.[13] The dimolecular nature of the base is shown by the fact that it yielded with methyl iodide a crystalline monomethiodide $(C_{18}H_{22}O_2N)_2CH_3I$, which could be further transformed into a dimethiodide (amorphous), $(C_{18}H_{22}O_2N \cdot CH_3I)_2$. For the amorphous base, which we may call bis-dihydrodesoxycodeine, the formula IV seems most probable.




IV. Bis-dihydrodesoxycodeine

Freund[14] describes the electrolytic reduction of bis-dihydrodesoxycodeine to the so-called $\alpha$-tetrahydrodesoxycodeine. We find pure bis-dihydrodesoxycodeine entirely unaffected by prolonged electrolytic reduction, and believe that the product which Freund observed (yield not stated) was actually tetrahydrodesoxycodeine,[15] formed through electrolytic reduction of small amounts of dihydrodesoxycodeine-D present as an impurity in his amorphous base. As we have shown,[2] dihydrodesoxycodeine-D can be reduced quantitatively to tetrahydrodesoxycodeine by the electrolytic method.

With the establishment of the dimolecular nature of the amorphous non-phenolic base, the necessity for the assumption of stereoisomers of formula II is eliminated.

A satisfactory explanation of the different courses taken in the reduction of the halogenocodides cannot be given at present. In the reduction of $\alpha$-chlorocodide, bromocodide and iodocodide where bis-dihydro-

[13] Busch and Schmidt, *Ber.*, **62**, 2612 (1929).

[14] Freund, *J. prakt. Chem.*, **101**, 36 (1921).

[15] Ochiai, *J. Pharm. Soc. Japan*, **578**, 58, April (1930), states that he was able to obtain tetrahydrodesoxycodeine by electrolytic reduction of the amorphous base, but does not mention the purity of his starting material nor the yield of tetrahydro product.

desoxycodeine or dihydrodesoxycodeine-D are the main products, it must be assumed that the first step in the reduction is elimination of the halogen atom. This can take place in two ways: removal of halogen as hydrogen halide, with simultaneous linking of two molecules of base to the dimolecular product, or formation of hydrogen halide and saturation of the valence at C-6 with hydrogen. As a second step in both cases, apparently, saturation of the double linkage still present in Ring III gives the end-products, bis-dihydrodesoxycodeine and dihydrodesoxycodeine-D, respectively. Attempts to isolate the hypothetical intermediate product resulting from the first step failed; when the reduction was stopped after one mole of hydrogen had been absorbed, oily, undistillable products were obtained. It is significant, however, that in every such case the whole reduction product was completely soluble in water. None of the bases in the halogenocodide or desoxycodeine series are soluble in water; therefore the whole of the first mole of hydrogen must have gone to form hydrogen halide as hypothesized above, which united with the base to give the water-soluble salt. That a dihydrohalogenocodide cannot be the first product could also be shown by direct experiment, for it was found impossible to eliminate the halogen from chlorodihydrocodide (*ex* dihydrocodeine) by catalytic reduction.[16] Whether α-chlorocodide reduces to bis-dihydrodesoxycodeine or to dihydrodesoxycodeine-D depends to a certain extent upon the speed of reduction. A large amount of catalyst or a more active catalyst favors formation of the dimolecular product.

β-Chlorocodide behaves in quite a different manner. Whereas in the case of the α-isomer tetrahydrodesoxycodeine appears only in traces (maximum 5%), under the same conditions β-chlorocodide yields about 30% of the tetrahydro product, and in the case of a very active catalyst, as platinum oxide, tetrahydrodesoxycodeine is the only product of the reduction. In no case could the dimolecular base be detected.

The fact that dihydrodesoxycodeine-D cannot be further reduced catalytically shows that the formation of tetrahydrodesoxycodeine does not take place through the reduction of this as an intermediate, but that the two products are formed by two different independent reduction processes. This is further supported by the experimental fact that the reduction which at completion would yield tetrahydrodesoxycodeine alone, with absorption of three molecules of hydrogen, when stopped after one mole of hydrogen had been used, yielded two-thirds unchanged β-chlorocodide and one-third tetrahydrodesoxycodeine hydrochloride.

It is not possible to give a plausible explanation of the different courses taken by the reduction in the cases of α- and β-chlorocodide. Speculations in regard to a reaction mechanism can have but little value until some direct evidence can be found to show whether or not the halogen in the α- and

[16] *Cf.* Ref. 6, p. 298.

TABLE I

CATALYTIC REDUCTION OF THE HALOGENOCODIDES

The time shown in this table is that required for complete reduction. In those cases where platinum oxide was used as the catalyst the reduction proceeded very rapidly and was practically complete in one-third of the time shown. During the remainder of the time indicated, the absorption was very slow, and finally stopped completely.

| Expt. | Base | Amount, g. | Catalyst | Amount, g. | Solvent | Amount, cc. | Moles $H_2$ absorbed | Time in hours | Dihydro-D, % | Tetrahydro- % | Bis-dihydro- % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | α-Chlorocodide | 15.0 | Pd–$BaSO_4$ | 4.0 | Dil. HCl, slight excess | 150 | 2.0 | 5.0 | 97 | .. | ... |
| 2 | α-Chlorocodide | 7.0 | Pd–$BaSO_4$ | 2.5 | Dil. HCl, slight excess | 100 | 2.0 | 2.0 | 90 | 5 | Trace |
| 3 | α-Chlorocodide | 5.0 | Pd–$BaSO_4$ | 3.0 | Dil. HCl, slight excess | 100 | 1.9 | 1.2 | 40 | 5 | 45 |
| 4 | α-Chlorocodide | 2.0 | Pd–$CaCO_3$ | 0.5 | Ethyl alcohol | 30 | 1.9 | 1.5 | Trace | Trace | 95 |
| 5 | α-Chlorocodide | 2.0 | Pd–$CaCO_3$ | .5 | Ethyl alcohol | 30 | 2.0 | 1.0 | .. | ... | 100 |
| 6 | α-Chlorocodide | 5.0 | $PtO_2$ | .2 | Ethyl alcohol | 35 | 1.85 | 0.5 | .. | ... | 95 |
| 7 | α-Chlorocodide | 10.0 | $PtO_2$ | .3 | Ethyl alcohol | 100 | 1.80 | 1.3 | .. | ... | 93 |
| 8 | α-Chlorocodide | 10.0 | $PtO_2$ | .3 | Ethyl alcohol | 100 | 1.80 | 1.3 | .. | ... | 95 |
| 9 | α-Chlorocodide | 1.0 | Pd colloidal | .06 | Dil. HCl, slight excess | 25 | 2.0 | 2.0 | 95 | ... | ... |
| 10 | β-Chlorocodide | 3.0 | Pd colloidal | .06 | Dil. HCl, slight excess | 30 | 2.25 | 5.6 | 73 | 22 | ... |
| 11 | β-Chlorocodide | 2.0 | Pd–$CaCO_3$ | 1.0 | Ethyl alcohol | 30 | 2.30 | 0.7 | 70 | 30 | ... |
| 12 | β-Chlorocodide | 3.2 | $PtO_2$ | 0.1 | Ethyl alcohol | 30 | 3.0 | 1.0 | .. | 100 | ... |
| 13 | β-Chlorocodide | 1.0 | $PtO_2$ | .1 | Methyl alcohol | 25 | 3.0 | 0.6 | .. | 100 | ... |
| 14 | Bromocodide | 3.0 | Pd–$BaSO_4$ | .75 | Dil. HCl, slight excess | 50 | 1.95 | 3.5 | 94 | Trace | ... |
| 15 | Bromocodide | 3.0 | $PtO_2$ | .15 | Ethyl alcohol | 30 | 2.1 | 6.0 | .. | ... | 100 |
| 16 | Bromocodide | 3.0 | Pd–$CaCO_3$ | .7 | Ethyl alcohol | 30 | 1.9 | 1.5 | .. | ... | 93 |
| 17 | Iodocodide | 2.0 | Pd–$BaSO_4$ | .5 | Dil. HCl, slight excess | 35 | 2.2 | 2.0 | 70 | ... | 25 |

β-isomers actually is located at the same point in the molecule. The relative inactivity usually shown by the chlorine atom in β-chlorocodide[17] is not displayed in the catalytic reductions described in this paper.

## Experimental

The α- and β-chlorocodides and iodocodide used in these experiments were prepared and purified as described in the first paper of this series.[18] The bromocodide was prepared according to the method of Schryver and Lees[19] from codeine and phosphorus tribromide, and showed the melting point 162°. The catalysts used, platinum oxide, colloidal palladium, palladium on barium sulfate and palladium on calcium carbonate were prepared by the usual methods.[20] The dihydrodesoxycodeine-D used as a test substance was prepared from β-chlorocodide by Mannich's procedure, and purified through the acid tartrate. The melting point of the free base, 106–107°, was not changed by distillation in high vacuum.

*Anal.* Calcd. for $C_{18}H_{23}O_2N$: C, 75.74; H, 8.12. Found: C, 75.85; H, 7.97.

The tetrahydrodesoxycodeine used for comparison was obtained from the catalytic hydrogenation of desoxycodeine-B.[21] It sintered at 131–132°, melted at 145–147° and evolved gas at 151°. The anhydrous form obtained from it by sublimation melted sharply at 157°.[9]

**Experiments 1, 2, 9 and 14,** in which dihydrodesoxycodeine-D was the chief product of reduction: the reaction mixtures were freed of the catalyst, treated with excess of dilute ammonia and the oily base extracted with ether. The ether yielded on distillation a nearly colorless oil, which solidified on standing to a mass of white crystals. The crude product was converted to the sparingly soluble acid tartrate by treating with a concentrated solution of the calculated amount of tartaric acid and adding boiling water until solution was complete. On cooling the solution slowly, the salt separated as fine white needles. The pure free base was obtained by treating the salt with ammonia and extracting into ether, and melted at 105–107°. It was identified in every case by mixed melting point, rotation ($[\alpha]_D^{20}$ −80.0° to −80.8°), and by the rotation of its acid tartrate ($[\alpha]_D^{25}$ −37.5° to −38.4°). In Experiment 2 a small amount of tetrahydrodesoxycodeine was recovered from the filtrate from the preparation of the acid tartrate.

**Experiments 4, 5, 6, 7, 8, 15 and 16,** in which bis-dihydrodesoxycodeine was the principal product of reduction: the reaction mixture was freed from catalyst, the alcoholic solution distilled, and the oily residue dissolved in 50 cc. of water. The base was liberated with a slight excess of dilute ammonia and extracted into ether, which left a light yellow oil on distillation. Small test portions in each experiment were heated to 200° in high vacuum, but only in the case of Experiment 4 did any material distil. This was small in amount and appeared to be a mixture of dihydrodesoxycodeine-D and tetrahydrodesoxycodeine.

**Experiments 3, 10, 11 and 17,** in which mixtures of two or three products were obtained: the mixed bases were liberated and brought into ether solution as described

[17] See for example, Small and Cohen, THIS JOURNAL, **53**, 2216, note 13 (1931).

[18] Ref. 17, p. 2214.

[19] Schryver and Lees, *J. Chem. Soc.*, **79**, 563 (1901).

[20] Platinum oxide, Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923); colloidal palladium, Skita, *Ber.*, **45**, 3579 (1912); palladium on barium sulfate, Schmidt, *ibid.*, **52**, 409 (1919); Rosenmund, *ibid.*, **51**, 585 (1918); palladium on calcium carbonate, Busch and Stöve, *ibid.*, **49**, 1064 (1916).

[21] Small and Cohen, THIS JOURNAL, **53**, 2225 (1931).

above, and the residue from distillation of the ether was distilled in high vacuum at 140–150°. Dihydrodesoxycodeine-D and tetrahydrodesoxycodeine distilled together as a colorless oil, and were separated by treatment with tartaric acid. The non-volatile residue consisted of bis-dihydrodesoxycodeine, which was identified in every case by conversion to the monomethiodide.

**Experiments 12 and 13,** in which tetrahydrodesoxycodeine was the only product: the free base obtained from distillation of the ether was dissolved in boiling alcohol, and water added until crystallization started. The yield of pure tetrahydrodesoxycodeine was in each case quantitative.

**Bis-dihydrodesoxycodeine.**—The amorphous base, the α-dihydrodesoxycodeine of Freund, was obtained from the reductions described above as a pale yellow, glass-like solid, exceedingly soluble in ether and in most organic media excepting petroleum ether and ligroin. It dissolved readily in acids and was precipitated unchanged by addition of alkali. From no solvent could it be obtained crystalline, nor did it yield any crystalline salts with a great variety of acids. In alcoholic solution it showed the rotation $[\alpha]_D^{26}$ −113.3°: $c = 3.344$, $l = 1$, $\alpha = -3.79°$. The monomethiodide was the only crystalline derivative which could be prepared. The amorphous product from the reduction of 10 g. of α-chlorocodide was dissolved in 50 cc. of boiling benzene, the solution cooled, and 10 g. of methyl iodide added, with constant stirring. An amorphous precipitate began to form immediately, with evolution of heat. The precipitation was complete in ten minutes and the amorphous methiodide was filtered out and washed with benzene. The yield was 11.2 g. The crude methiodide is unstable toward heat and decomposes to a black tar when warmed in most organic solvents. It was dissolved in cold alcohol and 10 volumes of acetone added; after the solution had stood for several days, long white needles separated. The monomethiodide softens and turns red at 200–230°, and melts with decomposition at 246–250°.

*Anal.* Calcd. for $C_{37}H_{47}O_4N_2I$: C, 62.51; H, 6.67; I, 17.87. Found: C, 62.69; H, 6.73; I, 18.08, 18.37, 17.83, 17.98 (samples for iodine determination were derived from four different experiments). In alcoholic solution the monomethiodide showed the rotation $[\alpha]_D^{23}$ −8.6°: $c = 2.256$, $l = 2$, $\alpha = -0.39°$.

On treatment with silver chloride the monomethiodide yielded the monomethochloride in the form of a yellow, glass-like solid which could not be crystallized.

**Bis-dihydrodesoxycodeine dimethiodide** was prepared by heating 2 g. of the monomethiodide in a sealed tube with 6 cc. of methyl iodide at 100° for two hours. The product was a reddish oil which gradually hardened to a glass, and could not be obtained crystalline. Like the monomethiodide, it decomposed when heated in solvents, but could be purified by dissolving in warm ethyl alcohol and precipitating with acetone. It separated as a fine white powder, which was apparently not crystalline, and melted at 230–250° with gradual decomposition.

*Anal.* Calcd. for $C_{38}H_{50}O_4N_2I_2$: C, 53.51; H, 5.91; I, 29.77. Found: C, 53.71; H, 5.97; I, 29.43, 29.40. In benzyl alcohol the dimethiodide showed the rotation $[\alpha]_D^{28}$ −71.5°: $c = 1.776$, $l = 1$, $\alpha = -1.27°$.

**Electrolysis of Bis-dihydrodesoxycodeine.**—The sample used in this experiment was obtained by catalytic reduction of α-chlorocodide in the presence of platinum oxide. A small test portion yielded no trace of distillable material when heated in high vacuum at 200°. Eight and one-half grams of the base was dissolved in 120 cc. of 20% sulfuric acid and electrolyzed, using a current of 13 amp. and an electrode of 60 sq. cm. The temperature was maintained between 10 and 20°, and the electrolysis continued for eight hours. The clear yellow solution was cooled to 0°, ether added, and a slight excess of ammonia. From the ether a reddish oil was obtained, which gave off no volatile bases at 200° in high vacuum. This excludes with certainty the presence of any di-

hydrodesoxycodeine-D or tetrahydrodesoxycodeine. The product from the attempted electrolytic reduction was unchanged bis-dihydrodesoxycodeine, for with methyl iodide it gave a monomethiodide identical with that described above. In alcohol, $[\alpha]_D^{24}$ $-8.4°$: $c = 2.190$, $l = 2$, $\alpha = -0.37°$.

*Anal.* Calcd. for $C_{37}H_{47}O_4N_2I$: I, 17.87. Found: I, 18.16.

**Partial Reduction of α-Chlorocodide.**—Three grams of α-chlorocodide in 30 cc. of ethyl alcohol was hydrogenated in the presence of 0.05 g. of platinum oxide. In twelve minutes one mole of hydrogen was absorbed and the reduction was interrupted. The solution was filtered, and the alcohol removed on the water-bath. The brown oily product obtained was completely soluble in water, and therefore must have consisted entirely of the hydrochloride of a new base. Treatment with ammonia and ether yielded a light yellow oil which slowly hardened to a glassy solid. It could not be obtained crystalline and gave no crystalline salts. It did not distil up to 200° at 1 mm., and at higher temperatures it decomposed.

**Partial Reduction of β-Chlorocodide.**—One gram of β-chlorocodide in 25 cc. of methanol was hydrogenated with 0.03 g. of platinum oxide as catalyst. In five minutes one mole of hydrogen was absorbed, and the experiment was stopped. The solution was filtered and two-thirds of the alcohol evaporated off. Slow addition of water to the hot solution precipitated a mass of large flake-like crystals. These proved to be pure β-chlorocodide, and weighed 0.6 g. The water-soluble portion from the reaction was treated with ammonia and ether, and yielded 0.25 g. of tetrahydrodesoxycodeine. The precipitation of one alkaloid exclusively from the alcoholic solution indicates that the two alkaloids must be of widely differing basicity. This is found to be the case by direct experiment. When water is added to an alcoholic solution of two moles of β-chlorocodide, one mole of tetrahydrodesoxycodeine and one mol of hydrochloric acid, the β-chlorocodide base is precipitated quantitatively and the tetrahydrodesoxycodeine remains in solution as the hydrochloride. Furthermore, when an ethereal solution of equimolecular amounts of β-chlorocodide and tetrahydrodesoxycodeine is extracted with sufficient hydrochloric acid to react with only one of the bases, only tetrahydrodesoxycodeine is extracted. The comparatively strong basic nature of tetrahydrodesoxycodeine may account in some degree for the peculiarity shown by its phenolic hydroxyl group.

## Summary

1. The contradiction presented in the supposed existence of the isomeric non-phenolic bases dihydrodesoxycodeine-D and α-dihydrodesoxycodeine has been removed with the discovery that the latter substance is dimolecular; it has been renamed bis-dihydrodesoxycodeine.

2. The catalytic hydrogenation of the halogenocodides has been studied. α-Chlorocodide yields principally dihydrodesoxycodeine-D or bis-dihydrodesoxycodeine, depending upon the catalyst. β-Chlorocodide yields only dihydrodesoxycodeine-D and tetrahydrodesoxycodeine. Bromocodide and iodocodide behave like α-chlorocodide.

UNIVERSITY, VIRGINIA

[CONTRIBUTION NO. 82 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

# DESOXYCODEINE STUDIES. IV. TETRAHYDRODESOXYCODEINE[1]

BY LYNDON F. SMALL AND FRANK L. COHEN

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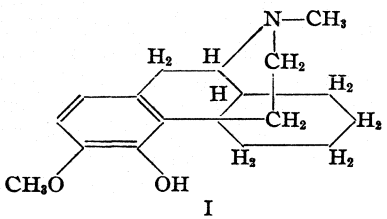
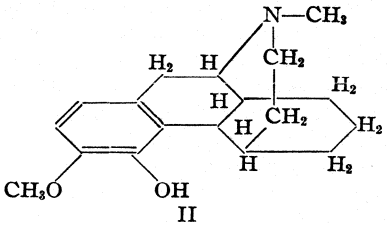
It has been shown in the previous papers of this series[2] that the end-product of reduction of all the known desoxycodeines (3) and dihydrodesoxycodeines (5) is a hydrated base, having the empirical formula $C_{18}H_{25}O_2N + {}^1/_2\ H_2O$, tetrahydrodesoxycodeine. The same compound may also be obtained directly from $\alpha$- or $\beta$-chlorocodide by catalytic reduction under special conditions.[3] The base formerly designated as $\alpha$-tetrahydrodesoxycodeine and for many years believed to be an isomer of the tetrahydrodesoxycodeine under consideration is actually a dihydrodesoxycodeine, dihydrodesoxycodeine-A.[4]

The generally accepted formulas for tetrahydrodesoxycodeine (I or II) represent it as a phenolic compound. Its remarkable insolubility in alkali and its indifference toward acetylation or benzoylation[5] and toward the usual methylating agents are difficult to bring into accord with such a structure.




I




II

Solid tetrahydrodesoxycodeine dissolves in dilute or concentrated alkali to the extent of about one part in 100,000, which is of the same order as its solubility in water. The base is extracted from its ethereal solution by alkali only to about the same degree. This insolubility in alkali is more striking in view of the fact that tetrahydrodesoxycodeine can be prepared from six different *alkali-soluble* desoxycodeines and dihydrodesoxycodeines by simple addition of hydrogen to a ring remotely removed from that which

[1] This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

[2] Small and Cohen, THIS JOURNAL, **53**, 2214, 2227 (1931).

[3] Mosettig, Cohen and Small, *ibid.*, **54**, 793 (1932).

[4] In this connection we wish to mention the statement of Ochiai and Hakozaki, *J. Pharm. Soc. Japan*, **578**, 58, April (1930) (omitted from *Chem. Abstracts*, **24**, 3793 (1930)) to the same effect.

[5] (a) Freund, *J. prakt. Chem.*, **101**, 29 (1921); (b) Mannich and Löwenheim, *Arch. Pharm.*, **258**, 304 (1920).

carries the hydroxyl group. As other investigators have observed,[5a,6] it is possible to dissolve tetrahydrodesoxycodeine in alkali under special conditions. Whereas slow addition of alkali to a solution of the base in hydrochloric acid causes complete and permanent precipitation, if the alkali be added in 200% excess and all at once, only a momentary cloudiness appears at the isoelectric point, and a perfectly clear solution results. This is, however, unstable or supersaturated, and after several minutes tetrahydrodesoxycodeine base separates in sparkling hexagonal plates. The final alkaline solution has an alkaloidal content of but one part in 5000.

While tetrahydrodesoxycodeine does not behave normally toward alkali, we have nevertheless been able to demonstrate the presence of the phenolic hydroxyl by the preparation of a methyl ether. The base does not methylate with diazomethane nor with phenyltrimethylammonium hydroxide[7] but reacts with methyl iodide in the presence of alkali to give a methyl ether methiodide.[8] By conversion of the methyl ether methiodide to the methochloride and distillation in high vacuum, the methyl ether itself is obtained as a colorless oil, which may be crystallized as the hydriodide.

The half molecule of water of crystallization which is normally present in tetrahydrodesoxycodeine (and notably in all the other phenolic bases of the desoxycodeine series) is readily removed when the base is distilled or sublimed in high vacuum. Anhydrous tetrahydrodesoxycodeine melts sharply at 123–124°, and slowly changes over into a second anhydrous form of m. p. 157–158°. Both forms show the same optical rotation in anhydrous benzene, and both are converted back to the hitherto known hydrated form by recrystallization from dilute alcohol or acetone. The anhydrous and hydrated bases give the same methiodide and the same salts.

Tetrahydrodesoxycodeine degrades readily by the method of A. W. Hofmann, and we have thus been able to establish a connection between the desoxycodeine series and the desoxymethylmorphimethines. Des-N-methyltetrahydrodesoxycodeine (III)[9] is formed in good yield when tetrahydrodesoxycodeine methiodide is boiled with strong alkali. The unsaturation established in the 9,10-position through the breaking of the nitrogen ring is readily saturated by catalytic hydrogen, yielding dihydro-des-N-methyltetrahydrodesoxycodeine (IV) which is identical in properties with dihydrodesoxytetrahydromethylmorphimethine. The latter substance was prepared by Cahn[10] through catalytic reduction of desoxytetrahydro-

[6] Kondo, *Ber.*, **63**, 646 (1930).

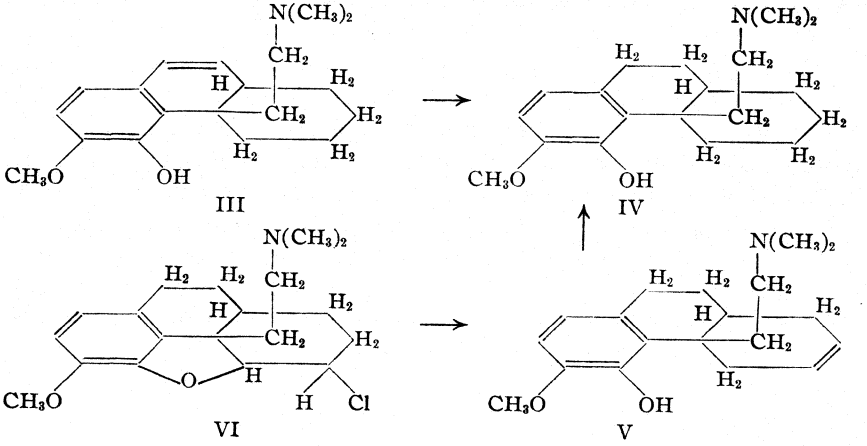
[7] Professor C. Schöpf, Darmstadt, states in a private communication that methylation of tetrahydrodesoxycodeine by the Rodionov method was successful.

[8] Freund, *J. prakt. Chem.*, **101**, 32 (1921).

[9] The optical antipode of this substance, des-N-methyldesoxydemethoxydihydrosinomenine, derived from the sinomenine series, has already been described by Goto and Mitsui, *Bull. Chem. Soc. Japan*, **6**, 33 (1931).

[10] Cahn, *J. Chem. Soc.*, 2562 (1926).

methylmorphimethine (V), the product which results when tetrahydrochloromethylmorphimethine (VI) is reduced with sodium and alcohol.



An attempt to arrive at the same result by degradation of dihydrodesoxycodeine-A was only partly successful. Dihydrodesoxycodeine-A methiodide, on boiling with alkali, gave a crystalline methohydroxide which was unexpectedly resistant to degradation and was at first mistaken for the methine base.[11] When the methohydroxide was boiled for a long time with strong alkali, ring scission took place to some extent, although the des-N-methyldihydrodesoxycodeine-A could not be isolated from the tarry product. The total degradation mass, on catalytic hydrogenation, yielded small amounts of the above-described dihydro-des-N-methyltetrahydrodesoxycodeine.

The unexpected alkali-insolubility noted for tetrahydrodesoxycodeine persists in its degradation products. Des-N-methyltetrahydrodesoxycodeine is precipitated from a 1% solution in N hydrochloric acid by excess of N alkali, and does not redissolve. It is present in the filtrate to the extent of about one part in 10,000. In 0.1% solution the same phenomenon is observed as in the case of tetrahydrodesoxycodeine: a clear solution is obtained temporarily, from which fine needles separate in the course of five minutes. Dihydro-des-N-methyltetrahydrodesoxycodeine, when precipitated from dilute acid by excess of alkali, is soluble in alkali to about 1:5000, but a temporarily clear alkaline solution could not be obtained under any conditions.

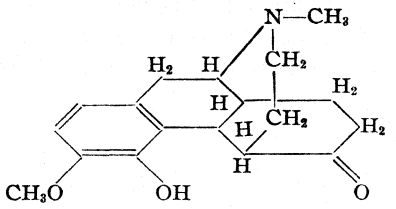
In 1920 Mannich[12] obtained by reduction of β-chlorocodide two alkali-insoluble bases, which he named dehydroxydihydrocodeine and dehydroxytetrahydrocodeine, respectively. The first of these we have already

[11] Small and Cohen, THIS JOURNAL, **53**, 2243 (1931).

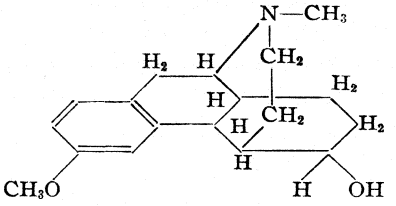
[12] Mannich and Löwenheim, *Arch. Pharm.*, **258**, 295 (1920).

described (dihydrodesoxycodeine-D), and have shown its relationship to other compounds in the desoxycodeine series.[13] The second, dehydroxytetrahydrocodeine, is identical with tetrahydrodesoxycodeine, a conclusion which was reached by Ochiai[14] while the present work was in progress. It is formed from β-chlorocodide by a mechanism different from that which results in dihydrodesoxycodeine-D, *i. e.*, it is not the product of further reduction of the latter, which is unaffected by catalytic reduction processes. The course which the reduction of β-chlorocodide takes is dependent in high degree upon the nature of the catalyst, as was demonstrated in the preceding paper of this series.

When the phenolic base dihydrothebainone (VII) is reduced electrolytically, a product is obtained which was named by its discoverers[15] dihydrothebacodine and was assigned formula VIII.




VII




VIII

The base was insoluble in alkali and could not be methylated, and showed a great similarity to the Mannich dehydroxytetrahydrocodeine. The presence of an alcoholic hydroxyl group could be shown by reaction with phosphorus pentachloride, which resulted in the well-crystallized chlorodihydrothebacodide. In a repetition of the Speyer experiment, we have been able to obtain by electrolytic reduction of dihydrothebainone only tetrahydrodesoxycodeine, in quantitative yield. The properties of this and of its salts correspond in every way with the description given of dihydrothebacodine and its derivatives,[16] and the des-N-methyl base from it likewise has the same properties as Speyer's des-N-methyldihydrothebacodine.[17]

[13] Small and Cohen, THIS JOURNAL, **53**, 2235 (1931).

[14] Ochiai, *J. Pharm. Soc. Japan*, **568**, 91, June (1929); Kondo and Ochiai, *Ber.*, **63**, 646 (1930); experimental proof not given.

[15] Speyer and Siebert, *Ber.*, **54**, 1519 (1921); C-15 is linked to C-5 in the Speyer formulas in accord with the formula of Knorr and Hörlein for morphine.

[16] The discrepancy of 100° in the melting point of the hydriodides, probably due to a misprint, has already been noted by Kondo, *Ann.*, **470**, 224 (1929). Kondo and Ochiai [*Ber.*, **63**, 646 (1930); Ochiai, *J. Pharm. Soc. Japan*, **568**, 91, June (1929)] published the statement that the two bases are probably identical before the experiments here described were completed. In view of the convincing evidence advanced by Speyer for the presence of an alcoholic hydroxyl group in dihydrothebacodine, this identity seemed improbable, and our experiments were therefore continued to a conclusion.

[17] Goto and Mitsui, *Bull. Chem. Soc. Japan*, **6**, 33 (1931), attacking the problem of

The product which we obtain from the electrolytic reduction of dihydrothebainone, like known samples of tetrahydrodesoxycodeine, is practically indifferent toward phosphorus pentachloride. About 90% of the material was regained unchanged; the remaining 10% consisted of a halogen-free amorphous product, which was insoluble in practically all organic solvents and gave no crystalline salts. It did not resemble chlorodihydrothebacodide in any way. In spite of the striking similarity in properties of dihydrothebacodine and tetrahydrodesoxycodeine and their derivatives, and of our failure to duplicate the Speyer and Siebert results, there can be no doubt that these investigators had in their hands a product which chlorinated smoothly and hence must have been different from tetrahydrodesoxycodeine. Until a direct comparison of the original Speyer dihydrothebacodine preparation with tetrahydrodesoxycodeine can be made, any decision concerning the identity of the two must be reserved.

The pharmacological action of tetrahydrodesoxycodeine and of the other bases of the desoxycodeine series has been investigated at the Pharmacological Laboratory of the University of Michigan and will be described in publications from that Institute.

We wish to acknowledge our indebtedness to Merck and Co., Rahway, N. J., who generously supplied us with the thebaine used in this research.

## Experimental

**Tetrahydrodesoxycodeine.**—The appearance of tetrahydrodesoxycodeine as the end-product of reduction of ten different bases was demonstrated in the second paper of this series.[18] Its formation through Clemmensen reduction of dihydrocodeinone[19] or of dihydrothebainone[20] should also be noted. The hydrated form which is always obtained when the base is crystallized from the ordinary organic solvents does not have a sharp melting point, but sinters down and becomes liquid between 141 and 147°, depending upon the rate of heating. Exhaustive fractional crystallization does not change the melting point or rotation. The anhydrous base which is first obtained by vacuum sublimation of the hydrate melts at 123–124°, and after several months changes to the second anhydrous form melting at 157–158°. After the second form appeared, the lower melting form could no longer be obtained.

**Tetrahydrodesoxycodeine Hemihydrate.**—*Anal.* Calcd. for $C_{18}H_{25}O_2N + {}^1/_2 H_2O$: C, 72.92; H, 8.84; $H_2O$, 3.02. Found: C, 72.85; H, 8.81; $H_2O$, 3.47, 3.08. In 95% alcohol, $[\alpha]_D^{20}$ −32.4°: $c = 1.883$, $l = 1$, $\alpha = -0.61°$. In dry benzene, $[\alpha]_D^{19}$ −66.0°, −67.8°: $c = 1.666, 1.834$, $l = 1, 2$, $\alpha = -1.10°, -2.49°$.

Freund describes tetrahydrodesoxycodeine as crystallizing from alcohol with one-half molecule of alcohol. We have analyzed numerous samples crystallized in this way, but have never found anything excepting the hemihydrate.

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the identity of the two bases in question by way of the sinomenine series, found that the des-N-methyl base from desoxydemethoxydihydrosinomenine (*d*-tetrahydrodesoxycodeine) melts at the same point as that given for des-N-methyldihydrothebacodine.

[18] Small and Cohen, THIS JOURNAL, **53**, 2238 (1931), diagram.

[19] Mannich and Löwenheim, *Arch. Pharm.*, **258**, 299 (1920).

[20] Ochiai, *J. Pharm. Soc. Japan*, **568**, 91, June (1929); also private communication from Dr. R. S. Cahn.

**Tetrahydrodesoxycodeine,** anhydrous, m. p. 123–124°.—*Anal.* Calcd. for $C_{18}H_{25}O_2N$: C, 75.22; H, 8.76. Found: C, 75.16, 75.31; H, 8.89, 8.76. In dry benzene, $[\alpha]_D^{18}$ −72.0°, −72.3°: $c = 1.826$, $l = 2, 1$, $\alpha = -2.63°, -1.32°$.

The base can be recrystallized from dry petroleum ether without change in m. p. or rotatory power.

**Tetrahydrodesoxycodeine,** anhydrous, m. p. 157–158°.—*Anal.* Calcd. for $C_{18}H_{25}O_2N$: C, 75.22; H, 8.76. Found: C, 75.14; H, 8.91. In dry benzene, $[\alpha]_D^{21}$ −70.2°: $c = 1.930$, $l = 2$, $\alpha = -2.71°$. In 95% alcohol, $[\alpha]_D^{24}$ −33.6°: $c = 1.874$, $l = 1$, $\alpha = -0.63°$.

The solubility of tetrahydrodesoxycodeine in water and in alkali was determined by a comparison of the precipitate formed by Mayer's reagent (potassium mercuric iodide) in acid solutions of known strength, with that produced in the test solution after filtering out excess base and acidifying. The base can be estimated easily down to dilutions of 1:100,000 by this method. The same procedure was used in determining the solubility of the degradation products of tetrahydrodesoxycodeine.

**Tetrahydrodesoxycodeine Derivatives.**—The derivatives listed below were analyzed by Freund. We have completed his description by determinations of the rotatory power: hydrochloride, large white prisms, m. p. 260–262°; in water, $[\alpha]_D^{20}$ −23.5°: $c = 2.509$, $l = 1$, $\alpha = -0.59°$. Hydriodide, long yellow needles, m. p. 245–246° (decomp.); in 95% alcohol, $[\alpha]_D^{19}$ −24.3°: $c = 2.360$, $l = 2$, $\alpha = -1.15°$. Methiodide, m. p. 260–263°; in water, $[\alpha]_D^{26}$ −33.3°: $c = 1.800$, $l = 1$, $\alpha = -0.60°$.

**Tetrahydrodesoxycodeine Methyl Ether.**—Fifteen grams of tetrahydrodesoxycodeine in 70 cc. of methyl alcohol was treated with 1.85 g. of sodium in 30 cc. of methyl alcohol, and to the resulting deep purple solution 17.0 g. of methyl iodide was added with strong cooling. The mixture was warmed slowly, refluxed for an hour, and evaporated on the water-bath to 30 cc. On slow addition of ether to the cold solution, tetrahydrodesoxycodeine methyl ether methiodide separated crystalline. It was recrystallized four times from methyl alcohol–ether mixture, yield 14 g.; m. p. 256–257°; $[\alpha]_D^{21}$ −3.54°: $c = 1.691$ (alcohol), $l = 1$, $\alpha = -0.06°$. The same compound was obtained by treatment of tetrahydrodesoxycodeine methyl ether (see below) with methyl iodide.

*Anal.* Calcd. for $C_{20}H_{30}O_2NI$: C, 54.15; H, 6.82; I, 28.64. Found: C, 54.23; H, 6.69; I, 28.39.

Twelve grams of tetrahydrodesoxycodeine methyl ether methiodide was dissolved in 400 cc. of water, and 6.8 g. of freshly precipitated silver chloride added at 70–80° with mechanical stirring. At the end of one hour at this temperature the reaction was finished, and the pale yellow solution obtained after filtering was evaporated to dryness in vacuum at 60°. The reddish gum so obtained was dissolved in 30 cc. of boiling acetone, filtered and concentrated to about 10 cc. After long standing in an ice-bath, the methochloride separated as a mass of fine white crystals, which were filtered off and washed with cold acetone. The yield was 7.1 g. of tetrahydrodesoxycodeine methyl ether methochloride, m. p. 255–256° (decomp.); $[\alpha]_D^{22}$ −9.5°: $c = 2.63$ (water), $l = 1$, $\alpha = -0.25°$.

*Anal.* Calcd. for $C_{20}H_{30}O_2NCl$: C, 68.22; H, 8.59; Cl, 10.08. Found: C, 68.29; H, 8.55; Cl, 10.01.

Six grams of the methochloride was distilled at 0.4 mm. pressure in a Pyrex tube having two 3-cm. bulbs. The decomposition of the methochloride began at about 250° (air-bath temperature) and was quite vigorous. Tetrahydrodesoxycodeine methyl ether distilled as a red oil, considerable tarry material remaining in the distilling bulb. After distilling twice more in vacuum, the compound was obtained as a colorless oil of disagreeable odor, which could not be induced to crystallize. The hydriodide crystallized

well from water, but the free base liberated from the pure hydriodide as a colorless, odorless oil did not crystallize.

*Anal.* Calcd. for $C_{19}H_{27}O_2N$: C, 75.69; H, 9.04. Found: C, 75.58; H, 9.15.

Tetrahydrodesoxycodeine methyl ether united with methyl iodide to give the methiodide of m. p. 256–257° described above.

Tetrahydrodesoxycodeine methyl ether hydriodide crystallizes from water in light brownish yellow needles sintering at 97–100°, melting at 217–218°; $[\alpha]_D^{21}$ −21.8°: $c = 2.011$ (alcohol), $l = 1$, $\alpha = -0.44°$.

*Anal.* Calcd. for $C_{19}H_{28}O_2NI + H_2O$: C, 50.98; H, 6.76; I, 28.37; $H_2O$, 4.02. Found: C, 50.65, 50.65; H, 6.63, 6.74; I, 28.24; $H_2O$, 3.79.

**Des-N-methyltetrahydrodesoxycodeine.**—Tetrahydrodesoxycodeine methiodide (4.8 g.) was boiled with 50 cc. of 50% potassium hydroxide solution for fifteen minutes. The oily reaction product solidified to a black cake when the solution was cooled. The solid was dissolved in hot alcohol and filtered; slow addition of water to the hot filtrate precipitated the base as sparkling flaky crystals. It was recrystallized from dilute alcohol and showed m. p. 152–154°; yield, 3.36 g., 87% of the calcd. amount. In methyl alcohol, $[\alpha]_D^{24}$ +66.2°: $c = 2.478$, $l = 1$, $\alpha = +1.64°$. The value was not permanent, and the solution turned red on standing. In hydrochloric acid (neutral solution) $[\alpha]_D^{20}$ +58.8°, +61.3°: $c = 4.124$, $l = 2, 1$, $\alpha = +4.85°$, +2.53°.

*Anal.* Calcd. for $C_{19}H_{27}O_2N$: C, 75.69; H, 9.02. Found: C, 75.83; H, 9.02.

**Dihydro-des-N-methyltetrahydrodesoxycodeine.**—Two grams of des-N-methyltetrahydrodesoxycodeine dissolved in 6 cc. of *N* hydrochloric acid and 20 cc. of water was hydrogenated in the presence of 0.2 g. of palladium–barium sulfate. One mol of hydrogen (170 cc.) was absorbed in one hour. The reaction mixture, in which the hydrochloride of the new base had begun to crystallize, was heated to boiling and filtered. The hydrochloride crystallized as short white needles from the cold solution; a second crop of crystals was obtained by concentrating the filtrate; the yield was quantitative. The salt melts at 251–252°, and is only sparingly soluble in cold water. In 95% alcohol, $[\alpha]_D^{26}$ −82.1°: $c = 1.425$, $l = 2$, $\alpha = -2.34°$.

*Anal.* (Subs. dried in vacuum at 135°) Calcd. for $C_{19}H_{30}O_2NCl$: Cl, 10.44. Found: Cl, 10.17.

The free base precipitated crystalline on addition of dilute ammonia to an aqueous solution of the hydrochloride. It was purified from dilute alcohol or acetone, and consisted of long white needles of m. p. 148–150°. In 95% alcohol, $[\alpha]_D^{26}$ −14.5°: $c = 1.720$, $l = 1$, $\alpha = -0.25°$.

*Anal.* Calcd. for $C_{19}H_{29}O_2N$: C, 75.20; H, 9.63. Found: C, 75.09; H, 9.75.

**Degradation of Dihydrodesoxycodeine-A.**—The methiodide of this base was boiled with 20 or 50% potassium hydroxide solution. According to the length of treatment the unchanged methiodide, the methohydroxide (crystalline, insoluble in ether or acetone but very soluble in water) or the des-N-methyl base was obtained. The extreme resistance of the methohydroxide to degradation is surprising. One hour's boiling with 50% potassium hydroxide was necessary to accomplish this, whereby much of the degradation product was destroyed. By hydrogenation of the tarry mass it was possible to isolate dihydro-des-N-methyltetrahydrodesoxycodeine because of its extraordinary tendency to crystallize. Des-N-methyldihydrodesoxycodeine-A itself could not be freed from the resinous by-products of the degradation.

**The So-called Dehydroxytetrahydrocodeine.**—The reduction of β-chlorocodide in the presence of palladium and the advantageous use of tartaric acid to separate the products was described in our second paper.[21] The tetrahydro product obtained did

[21] Small and Cohen, THIS JOURNAL, 53, 2242 (1931).

not depress the melting point of known samples of tetrahydrodesoxycodeine and yielded salts identical with those from this base. For the base we found $[\alpha]_D^{23}$ −32.9° (for tetrahydrodesoxycodeine, $[\alpha]_D^{21}$ −32.1°); the hydriodide melted at 241–243°, the methiodide at 260–265° and did not depress the melting points of the corresponding tetrahydrodesoxycodeine derivatives.

**Electrolytic Reduction of Dihydrothebainone.**—Two and one-half grams of dihydrothebainone in 150 cc. of 20% sulfuric acid was reduced for four hours with 8.8 amp. on a 60 sq. cm. prepared lead electrode; the temperature was kept below 20°. At the end of the reaction the mixture was filtered, treated with an excess of ammonia, and the reddish solid crystallized to constant m. p. from acetone; the yield was practically quantitative. It melted at 144–145° (dihydrothebacodine, 149°) and showed the characteristic behavior of tetrahydrodesoxycodeine toward alkali. It did not depress the melting point of tetrahydrodesoxycodeine, and sublimed to give the anhydrous form of this base, m. p. 123–124°, which changed to the second form, m. p. 157–158°, in several months. These anhydrous forms likewise showed no m. p. depression with known samples. The hydrated form had the rotation $[\alpha]_D^{21}$ −32.1° in alcohol, and gave a hydriodide and methiodide which were compared directly with known samples.

One gram of the dihydrothebainone reduction product in 6 cc. of chloroform with 1.0 g. of phosphorus pentachloride was allowed to stand at room temperature for two hours and then heated to reflux for a further two hours. Traces of hydrogen chloride were evolved during the heating. The cooled mixture was poured into 200 cc. of ether and the viscous mass which formed was separated from the liquid and treated with sodium carbonate solution. A tarry product was obtained which could be separated into two fractions with alcohol. The alcohol solution yielded most of the starting material unchanged. The alcohol-insoluble part (0.1 g.), m. p. about 200°, was halogen-free and was practically insoluble in all available solvents excepting pyridine. It dissolved in acids with difficulty and was reprecipitated by alkali; it formed an amorphous hydriodide, m. p. about 280°, and an insoluble tarry methiodide. Nothing corresponding to chlorodihydrothebacodide could be obtained from the reaction. A known sample of tetrahydrodesoxycodeine behaved in the same way in a parallel experiment.

## Summary

1. Tetrahydrodesoxycodeine has been prepared in two crystalline anhydrous modifications. The alkali-insolubility of the base has been studied, and the presence of a phenolic hydroxyl group demonstrated by the preparation of a methyl ether.

2. Through degradation of tetrahydrodesoxycodeine and hydrogenation of the product, a connection between the desoxycodeine and the tetrahydromethylmorphimethine series has been established.

3. The identity of tetrahydrodesoxycodeine with dehydroxytetrahydrocodeine and with dihydrothebacodine is discussed.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

# ROTENONE. XIX. THE NATURE OF THE ALKALI SOLUBLE HYDROGENATION PRODUCTS OF ROTENONE AND ITS DERIVATIVES AND THEIR BEARING ON THE STRUCTURE OF ROTENONE

BY F. B. LAFORGE AND H. L. HALLER

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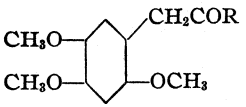
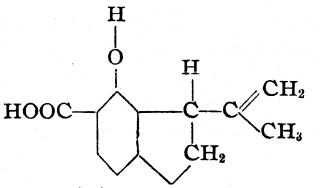
In the early investigations on the structure of rotenone Takei[1] suggested the presence of a lactone group, and Butenandt[2] believed that he had evidence of its presence in rotenol and also in rotenone because the latter gave an alkali-soluble compound on hydrogenation in ammoniacal solution. In the course of our earlier work, we obtained from a number of rotenone derivatives by hydrogenation in neutral solutions, alkali-soluble products which we believed to be acids.[3] We also observed that these products were of very weak acidic properties, were displaced from their salts by carbon dioxide, and could not be successfully titrated. It might have been suspected that they were phenols rather than acids, except for the complete absence of the ferric chloride color test.

After the structure of the methoxyl-containing part of derritol methyl ether had been established as (A)




(A)




(B)

and it was shown that this derivative behaved like rotenone and many of its related compounds with respect to hydrogenation and yielded a corresponding acid, it became evident that the grouping involved was located in the part of the molecule (R) which yielded tubaic acid.

From theoretical considerations it was impossible to reconcile the formula for tubaic acid postulated by Takei (B) or any similar scheme, with the presence of a lactone group in that part of the molecule, and we were therefore inclined to believe that tubaic and isotubaic acids were secondary reaction products in spite of the fact that they were always obtained on oxidation or alkali fusion of numerous rotenone derivatives. A general exception to this rule was the fact that none of the so-called acids obtained by hydrogenation gave tubaic, isotubaic or dihydrotubaic acid by either process.

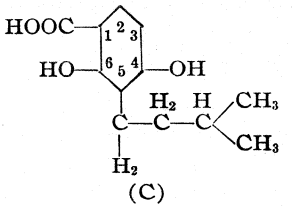
[1] S. Takei, *Biochem. Z.*, **157**, 1 (1925).

[2] A. Butenandt, *Ann.*, **464**, 253 (1929).

[3] To avoid confusion the names of the alkali-soluble hydrogenation products originally termed acids are retained.

We have now made a further study of the hydrogenation products of tubaic acid on the one hand and of derrisic acid on the other, and the results apparently explain the nature of the alkali-soluble hydrogenation products of rotenone and its derivatives.

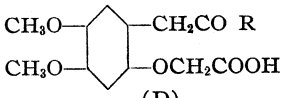
In our last communication[4] it was reported that tubaic acid is hydrogenated to a tetrahydro compound of formula $C_{12}H_{16}O_4$ which we proved to be a substituted dihydroxybenzoic acid, in all probability to be expressed by formula (C). Both hydroxyls in this compound are easily acetylated, but only one is easily methylated. From further considerations it is fairly certain that the hydroxyl in position 6 is the one which resists methylation, although it gives a strong color test with ferric chloride.



(C)

These results are strictly analogous to those which were obtained in a parallel study of derrisic acid.

Derrisic acid was correctly expressed in a previous communication[5] by the partial formula (D) in which R represented the tubaic acid part of the molecule, containing, as was supposed, the lactone group.



(D)

Derrisic acid was found to yield on hydrogenation under pressure a mixture of dihydro ($C_{23}H_{26}O_8$), and tetrahydro ($C_{23}H_{28}O_8$) derrisic acids. Like tetrahydrotubaic acid, the latter could be isolated owing to its insolubility in chloroform.

It was also found that the ethyl ester of derrisic acid readily yielded the same tetrahydro acid even at atmospheric pressure and that the ester of the tetrahydro acid could be separated from the dihydro ester by extracting the cold acetic ester solution of the mixture with aqueous alkali.

Thus it was found that derrisic acid undergoes the same reaction on hydrogenation as does rotenone.

Tetrahydroderrisic acid is optically inactive, gives a strong ferric chloride color test and is easily methylated by dimethyl sulfate with the formation of a methyltetrahydroderrisic acid methyl ester which separates in crystalline form from the alkaline solution during the process. Both the methyl ester and the corresponding acid give a color test with ferric chloride.

The presence of a free hydroxyl group in the methyl ester is also demonstrated by the formation of a mono acetyl derivative which gives no phenol test with ferric chloride.

Tetrahydroderrisic acid itself when boiled with acetic anhydride yields a

[4] Haller and LaForge, THIS JOURNAL, **53**, 4460 (1931).

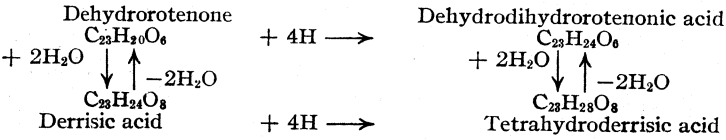
[5] LaForge, Haller and Smith, *ibid.*, **53**, 4400 (1931).

light yellow monoacetyl compound of formula $C_{25}H_{26}O_7$, which gives no phenol reaction. This compound is identical with the product obtained from dehydrodihydrorotenonic acid $C_{23}H_{24}O_6$, the alkali-soluble hydrogenation product of dehydrorotenone, by the same treatment. When the acetyl group is removed by saponification the original dehydrodihydrorotenonic acid is obtained.

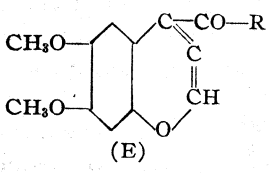
In a previous communication[6] we reported that this dehydrodihydrorotenonic acid yielded an acid of formula $C_{23}H_{26}O_7$ on treatment with zinc dust in alcoholic aqueous alkaline solution. A re-examination of this product showed that as ordinarily prepared it was always contaminated with a small quantity of starting material, which led to the erroneous analysis. The compound could, however, be easily purified by treatment with chloroform, which dissolves the dehydrodihydrorotenonic acid, leaving the pure compound which then analyzed for, and was identical with, tetrahydroderrisic acid, $C_{23}H_{28}O_8$. Tetrahydroderrisic acid is most easily prepared by the last-mentioned method.

Tetrahydroderrisic acid, therefore, by the action of acetic anhydride reverts through the acetyl derivative with loss of two moles of water to dehydrodihydrorotenonic acid. This is the reverse process of its formation by alkaline hydrolysis from dehydrodihydrorotenonic acid with addition of two moles of water.

An analogous behavior has been observed in the case of deguelic acid[7] which reverts to dehydrodeguelin by treatment with acetic anhydride. The same process occurs in the case of derrisic and isoderrisic acids, which are converted into dehydro and isodehydrorotenone by the same agent. These relations are expressed by the formulas in the following chart




Dehydrodihydrorotenonic acid is easily methylated, and the methylated compound is converted by alkaline hydrolysis into 4-methyltetrahydroderrisic acid, identical with the product obtained by methylation of tetrahydroderrisic acid.



(E)

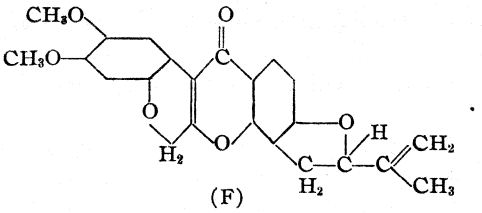
In one of our recent publications[5] we expressed the formula of dehydrorotenone by (E). This formula was open to serious objections, but it served to explain the characteristic reaction of the compound under the assumption that a lactone group was contained in the tubaic acid part of the molecule. It has now become evident that the

[6] LaForge and Smith, THIS JOURNAL, **52**, 3603 (1930).

[7] Clark, *ibid.*, **52**, 313 (1931).

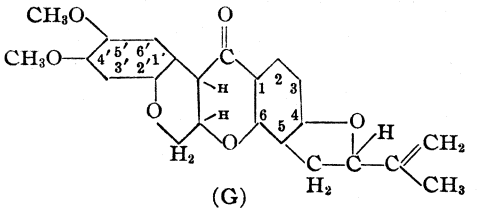
lactone group is not present in rotenone or any of its derivatives, and we now suggest an important modification of this formula based on the results described in this article.

Dehydrorotenone should now be expressed by the complete formula (F)



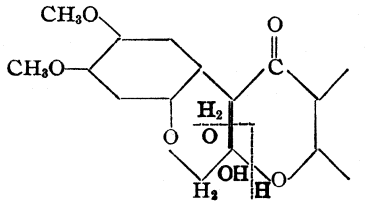
(F)

and it would be derived from rotenone (G) by loss of two hydrogen atoms.



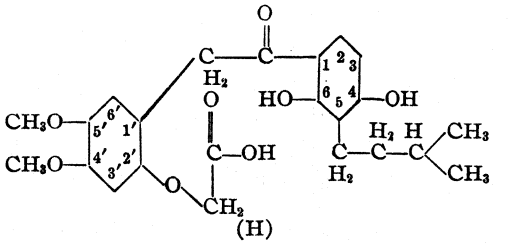
(G)

Derrisic acid is obtained from dehydrorotenone by the action of alcoholic alkali, the process being one of hydrolysis as follows



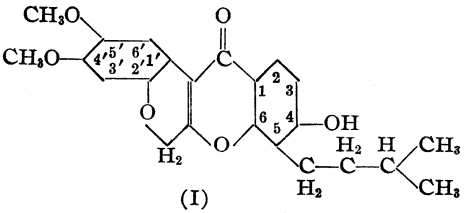
When derrisic acid is converted into dehydrorotenone by acetic anhydride, the reverse process, dehydration occurs.

Tetrahydroderrisic acid is now represented by the complete formula (H)



(H)

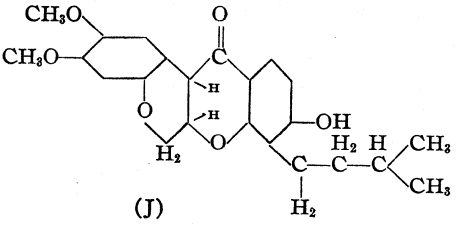
and dehydrodihydrorotenonic acid derived from it by dehydration by (I).



(I)

Dehydrodihydrorotenonic acid is acetylated in position 4 to form its acetyl derivative.

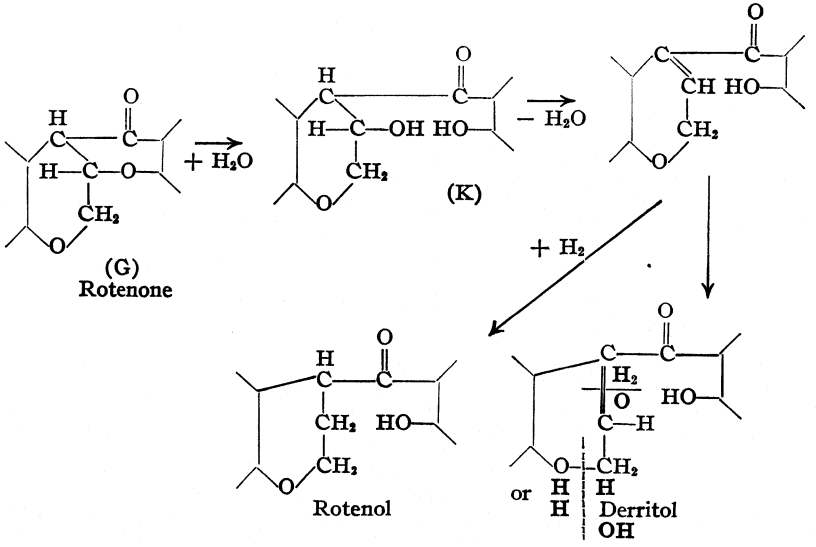
Dihydrorotenonic acid, which is obtained from rotenone (G) by hydrogenation, with opening of the oxide ring and loss of an asymmetric center would consequently be represented by formula (J). In tetrahydroderrisic



(J)

acid (H) the hydroxyl group in position 4 is easily methylated, but the one in 6 is not. The methyl ester of methylated tetrahydroderrisic acid is not soluble in alkali, but it is easily acetylated in position 6 under conditions which lead to the formation of dehydro compounds in cases where the carboxyl group is free.

Tetrahydroderrisic acid therefore contains two phenolic hydroxyl groups. The one in position 6 gives the ferric chloride color test as in the

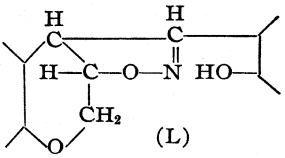


case of derrisic acid and certain other compounds, including rotenol, which contain the phenol group in this position.

The mechanism of the reactions leading to the formation of derritol and rotenol is with slight modification essentially the same as indicated in our previous article and are expressed by the preceding formulas.

Derritol is then a diphenol, and rotenol is a monophenol. This is in agreement with the observation that both derritol monomethyl ether and rotenol give phenol color reactions although both are insoluble in alkali. In fact, aside from the true acids containing the carboxyl group, all compounds so far observed are insoluble in alkali except those containing a free phenolic group in position 4 on the tubaic acid side (rotenonic acid) or one in position 2′ on the derric acid side (derritol). It is probable that the insolubility of those compounds containing only one free phenol group in position 6 is dependent on the presence of a carbonyl group in position 1 since rotenone isoxime and the related compounds are alkali soluble.[2]

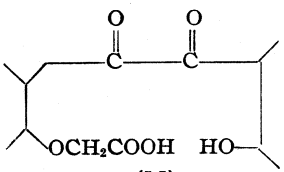
Rotenone isoxime would in all probability contain the grouping (L) and would be formed from the grouping (K) with loss of one molecule of water.



(L)

A renewed attempt to acetylate rotenol led to a product which gave no phenol reaction with ferric chloride, although it failed to crystallize.

As a further confirmation of the formula for derrisic acid we have prepared the corresponding 1,2-diketone from isoderrisic acid. Isoderrisic acid, as would be expected, reacted with nitrous acid to give a compound containing the grouping (M) indicated below.



(M)

It follows from the results described above that the rotenone molecule does in fact contain the nucleus of tubaic acid modified as to the point of attachment of the alkyl side chain as indicated in Formula D.

## Experimental

**Tetrahydroderrisic Acid.**—One gram of derrisic acid was reduced with 0.5 g. of active platinum catalyst in 40 cc. of acetic ester under 50 pounds pressure for about two hours. The solution was filtered, the solvent removed and the residue recrystallized from 50% alcohol.

The first product was a mixture of dihydro- and tetrahydroderrisic acids. The compound was obtained pure by repeated extraction of the mixture with chloroform, which left most of the tetrahydro derivative undissolved. It was finally recrystallized from 50% alcohol. It melted at 204–206° and gave a positive ferric chloride test. The yield was about 0.3 g.

*Anal.* Subs., 0.0688, 0.0758: $CO_2$, 0.1616, 0.1765; $H_2O$, 0.0405, 0.0443. Calcd. for $C_{23}H_{28}O_8$: C, 63.88; H, 6.48. Found: C, 64.08, 63.50; H, 6.54, 6.50.

The same compound was obtained by hydrogenation of derrisic acid ethyl ester at ordinary pressures. About the calculated volume of hydrogen was absorbed in a

few minutes, after which the acetic ester solution was cooled with ice and rapidly extracted with 2% potassium hydroxide solution.

The aqueous alkaline solution was allowed to stand for a few minutes at ordinary temperature to saponify the ester, and then acidified. The precipitated mixture, which contained very little of the dihydro compound, was filtered off, and recrystallized from 50% alcohol, and the dried material was extracted with chloroform and recrystallized from 50% alcohol. It melted at 204–206°.

**Tetrahydroderrisic Acid from Dehydrodihydrorotenonic Acid.**—Dehydrodihydrorotenonic acid was boiled with zinc dust in aqueous alcoholic potassium hydroxide solution as described in a previous article.[8] The resulting product (formerly called β-hydroxyrotenonic acid) was extracted with chloroform, which removed a small quantity of unchanged dehydrodihydrorotenonic acid. It was then recrystallized from 50% alcohol. It melted at 206°. It was shown by the mixed melting point and optical examination of the crystals to be identical with tetrahydroderrisic acid. The substance is obtained more easily and in better yield by this method. It was optically inactive.

*Anal.* Subs., 0.0745: $CO_2$, 0.1757; $H_2O$, 0.0433. Calcd. for $C_{23}H_{28}O_8$: C, 63.88; H, 6.48. Found: C, 64.31; H, 6.46.

**Ethyl Ester of Tetrahydroderrisic Acid.**—This derivative was obtained from tetrahydroderrisic acid prepared by both the above-mentioned methods. One part of the acid was boiled with twenty parts of absolute ethyl alcohol containing 1% of sulfuric acid, for half an hour. The ester separated on cooling and was recrystallized from 95% alcohol. It melted at 180°, gave a strong color test with ferric chloride and was easily soluble in dilute cold alkali.

*Anal.* Subs., 0.0802: $CO_2$, 0.1918; $H_2O$, 0.0460. Calcd. for $C_{25}H_{32}O_8$: C, 65.22; H, 6.96. Found: C, 65.22; H, 7.11.

**4-Methyltetrahydroderrisic Acid and 4-Methyltetrahydroderrisic Acid Methyl Ester.**—Four grams of tetrahydroderrisic acid was dissolved in 35 cc. of 5% potassium hydroxide solution. The solution was agitated with a mechanical stirrer while 7 g. of dimethyl sulfate was slowly added over a period of one-half hour. The agitation was continued for two hours, the solution being kept alkaline with further addition of alkali. The methyl ester of methyl tetrahydroderrisic acid separated in crystalline form from the alkaline solution. It was filtered off and recrystallized from methyl alcohol. In some experiments the crystals contained a gummy impurity which was easily washed off with methyl alcohol. It crystallized in stout heavy prisms. The yield was 2.5 g. The ester melted at 111–112°. The ferric chloride test was positive.

*Anal.* Subs., 0.0802 g., 3.345 mg.: $CO_2$, 0.1910, 8.010; $H_2O$, 0.0478, 2.076. Subs., 0.0207: cc. of thiosulfate (1 cc. = 0.000517 $CH_3O$),[9] 10.85. Calcd. for $C_{25}H_{32}O_8$: C, 65.21; H, 6.94; $4CH_3O$, 26.95. Found: C, 64.95, 65.30; H, 6.64, 6.89; $CH_3O$, 27.09.

The corresponding 4-methyltetrahydroderrisic acid was obtained by saponification of the ester. The alkaline solution obtained on methylation also contained the free acid, which was isolated by acidification and extraction with ether. The acid after recrystallizing from benzene melted at 158°. When it was again recrystallized from acetic acid, the melting point was 164°. It gave a positive test with ferric chloride.

*Anal.* Subs., 0.0797: $CO_2$, 0.1887; $H_2O$, 0.0472. Subs., 0.0211: thiosulfate solution (1 cc. = 0.000581 $CH_3O$), 7.56 cc.; 0.0215; thiosulfate solution (1 cc. = 0.000517 $CH_3O$), 8.65 cc. *Titration.* Subs., 0.0210: *N*/20 KOH, 1.00 cc. Calcd. for $C_{24}H_{30}O_8$: C, 64.57; H, 6.72; $3CH_3O$, 20.85; mol. wt. 446. Found: C, 64.57; H, 6.54; $CH_3O$, 20.77, 20.80; mol. wt. 420.

[8] La Forge and Smith, THIS JOURNAL, 52, 3606 (1930).

[9] F. Vieböck and Schwappach, *Ber.*, 63, 2818 (1930).

**6-Acetyl-4-methyltetrahydroderrisic Acid Methyl Ester.**—Seven-tenths of a gram of the ester was acetylated by boiling with 10 cc. of acetic anhydride containing 5% of acetic acid and 0.2 g. of sodium acetate. The boiling was continued for thirty minutes, after which methyl alcohol was added and the solution concentrated to about 5 cc. The product crystallized on addition of water and was recrystallized from methyl alcohol, from which it separates in long white needles. It melted at 111° and gave no phenol test with ferric chloride.

*Anal.* Subs., 0.0741: $CO_2$, 0.1763; $H_2O$, 0.0449. Subs., 0.0207: thiosulfate (1 cc. = 0.000517 $CH_3O$), 9.90 cc. Calcd. for $C_{27}H_{34}O_9$: C, 64.54; H, 6.77; $4CH_3O$, 24.70. Found: C, 64.88; H, 6.73; $CH_3O$, 24.72.

**Derric Acid from Methyltetrahydroderrisic Acid.**—Two grams of substance oxidized with 6 cc. of 30% hydrogen peroxide in 5% potassium hydroxide solution yielded 0.4 g. of derric acid. The melting point was 170°.

*Anal.* Subs., 0.0215: AgI, 0.0370. Calcd. for $C_{12}H_{14}O_7$: $2CH_3O$, 22.96. Found: $CH_3O$, 22.75.

**4-Acetyldehydrodihydrorotenonic Acid from Tetrahydroderrisic Acid.**—One-half gram of substance was boiled for ten minutes with 7 cc. of acetic anhydride containing 5% of acetic acid and 0.15 g. of anhydrous sodium acetate. An equal volume of alcohol was added, and the solution was boiled for a few minutes longer. On cooling the acetyl compound separated out in light yellow prismatic needles. It was recrystallized from alcohol, in which it is soluble with difficulty. It melted at 202° and gave no ferric chloride test. The yield was about 0.2 g.

*Anal.* Subs., 0.0823, 0.0783: $CO_2$, 0.2062, 0.1953; $H_2O$, 0.0429, 0.0422. Calcd. for $C_{25}H_{26}O_7$: C, 68.48; H, 5.91. Found: C, 68.33, 68.02; H, 5.73; 5.99.

**4-Acetyldehydrodihydrorotenonic Acid from Dehydrodihydrorotenonic Acid.**—One gram of dehydrodihydrorotenonic acid was boiled with 15 cc. of acetic anhydride, 1 cc. of acetic acid and 0.25 g. of anhydrous sodium acetate for fifteen minutes. An equal volume of alcohol was added, and the solution boiled for a few minutes. The substance was recrystallized from alcohol and melted at 202°. It was identical with the one obtained from tetrahydroderrisic acid described above, as determined by the mixed melting point and crystal form. The yield was 0.8 g.

*Anal.* Subs., 0.0710: $CO_2$, 0.1782; $H_2O$, 0.0371. Subs., 0.0227: AgI, 0.0245. Calcd. for $C_{25}H_{26}O_7$: C, 68.48; H, 5.91; $2CH_3O$, 14.13. Found: C, 68.45; H, 5.80; $CH_3O$, 14.26.

On saponification with alcoholic potassium hydroxide it yielded the original dehydrodihydrorotenonic acid.

**4-Methyldehydrodihydrorotenonic Acid.**—Two grams of dehydrodihydrorotenonic acid was dissolved with gentle warming in about 25 cc. of 5% potassium hydroxide. The solution was agitated with a mechanical stirrer and 6 cc. of dimethyl sulfate was added over a period of about one hour. The reaction was continued for another hour with further addition of alkali from time to time. The product separated crystalline during the process and was filtered off, washed with dilute alkali and recrystallized from alcohol. It formed long nearly white prisms melting at 169°.

*Anal.* Subs., 0.0814: $CO_2$, 0.2090; $H_2O$, 0.0460. Calcd. for $C_{24}H_{26}O_6$: C, 70.24; H, 6.34. Found: C, 70.02; H, 6.28.

**4-Methyltetrahydroderrisic Acid from 4-Methyldehydrodihydrorotenonic Acid.**—One gram of 4-methyldehydrodihydrorotenonic acid was refluxed in 90 cc. of alcohol with 10 cc. of 15% potassium hydroxide solution and 2 g. of zinc dust for four hours. The solution was then filtered into dilute hydrochloric acid solution. The precipitate was filtered off and dissolved in ether. The ether solution was extracted with dilute

alkali, and the alkaline extract was acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water and dried. It was recrystallized from glacial acetic acid. It melted at 163–164°. When it was mixed with an equal quantity of 4-methyltetrahydroderrisic acid the melting point was 162–163°.

*Anal.* Subs., 0.00248: thiosulfate (1 cc. = 0.000517 $OCH_3$), 10.10 cc. Calcd. for $C_{24}H_{30}O_8$: $3CH_3O$, 20.85. Found: 21.05.

**1,2-Diketone from Isoderrisic Acid.**—One and a half grams of isoderrisic acid was suspended in 12 cc. of glacial acetic acid, and cooled with an ice-bath, and 8 g. of amyl nitrite was added. Twelve cc. of a mixture of equal parts of concentrated hydrochloric and glacial acetic acid was added over a period of thirty minutes, and the solution was allowed to stand for several hours at room temperature. The isoderrisic acid gradually went into solution with slow gas evolution. Water was added, and the products were extracted with ether. The ether solution was washed with water to remove the acetic acid, and then with dilute sodium carbonate. The alkaline solution was acidified and extracted with ether. The ether residue crystallized on standing. It was washed with benzene and recrystallized from a small volume of glacial acetic acid, from which it separated in bright yellow heavy prisms. It contained solvent of crystallization which was expelled in vacuum at 100°. The yield was 0.5 g. It gave a positive ferric chloride test and melted at 195°.

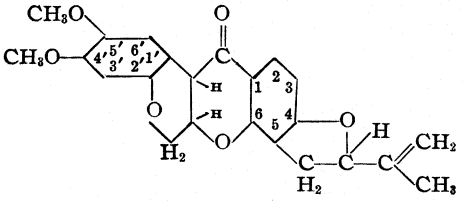
*Anal.* Subs., 0.0712: $CO_2$, 0.1631; $H_2O$, 0.0336. Subs., 0.02125: thiosulfate (1 cc. = 0.000517 $CH_3O$), 5.65 cc. Calcd. for $C_{23}H_{22}O_9$: C, 62.64; H, 4.98; $2CH_3O$, 14.02. Found: C, 62.46; H, 5.24; $CH_3O$, 13.74.

## Summary

Derrisic acid is hydrogenated to tetrahydroderrisic acid.

Tetrahydroderrisic acid is also obtained by alkaline hydrolysis of dehydrodihydrorotenonic acid. Conversely, by the process of dehydration, derrisic and tetrahydroderrisic acids are converted into dehydrorotenone and dehydrodihydrorotenonic acid.

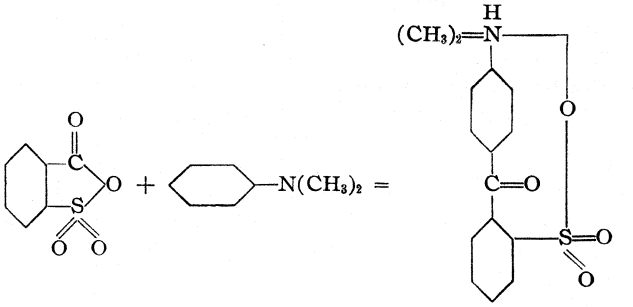
Both dehydrodihydrorotenonic acid and tetrahydroderrisic acid are phenols which can be methylated in position 4. Tetrahydroderrisic acid is a diphenol, and its ester can be acetylated in position 6. Derritol is a diphenol and rotenol a monophenol. All rotenone derivatives which have only one free phenol group in position 6 are alkali insoluble although they give a positive color test with ferric chloride. The lactone group is not present in rotenone or any of its derivatives, and the alkali-soluble hydrogenation products which were supposed to contain the carboxyl group are not acids but phenols. All the reactions of rotenone and its derivatives are now easily explained by the formula:




WASHINGTON, D. C.

## NOTES

**4[1]-Dimethylaminobenzophenone-2-sulfonic Acid.**[1]—In attempting to prepare dimethylanilinesulfonephthalein[2] from dimethylaniline and the anhydride of *o*-sulfobenzoic acid a substance was isolated which proved to be 4[1]-dimethylaminobenzophenone-2-sulfonic acid. This compound would be the so-called "intermediate acid" in the preparation of the sulfonephthalein from the anhydride.



The dry acid combines with ammonia, but not with hydrogen chloride. Its barium and ammonium salts were made. Attempts to prepare an acetyl derivative of a γ-lactone form failed. It is isomeric with 4[1]-dimethylaminobenzophenone-3-sulfonic acid.[3]

Dimethylaniline condenses similarly with phthalic acid anhydride, tetrachlorophthalic acid anhydride, 3,4-dichloro- and 3,4-dibromophthalic acid anhydrides.[4]

### Experimental Part

One mole (105 g.) of *o*-sulfobenzoic acid anhydride[5] was dissolved in 3 moles (208 g.) of freshly distilled, warm dimethylaniline. The solution was heated in an oil-bath at 110° for thirty hours. It became green and colorless crystals separated. After cooling, the supernatant liquid was poured off and the crystals were treated with

[1] This work was started at the suggestion of the late Professor W. R. Orndorff, who had hoped to investigate systematically the various amino derivatives in the sulfonephthalein series. As it seems improbable that the present author will continue the problem, this note is published.

[2] M. D. Sohon, *Am. Chem. J.*, **20**, 127, 257 (1898).

[3] R. Willstätter and M. Goldmann, *Ber.*, **39**, 3773 (1906).

[4] A. Haller and A. Guyot, *Compt. rend.*, **119**, 205 (1894); **126**, 1248, 1544 (1898); **132**, 746 (1901); *Bull. soc. chim.*, [3] **17**, 582 (1893); A. Haller and H. Umbgrove, *ibid.*, [3] **25**, 598, 745 (1901); *Compt. rend.*, **129**, 90 (1899); H. Limpricht and E. König, *Ann.*, **300**, 228 (1898); H. Limpricht and H. Seyler, *ibid.*, **307**, 305 (1899); J. Perard, *Compt. rend.*, **143**, 237 (1906); **146**, 934 (1908); *Ann. chim.*, [9] **7**, 340 (1917); **8**, 22 (1918); G. Cohn, *Pharm. Zentr.*, **55**, 735, 763 (1914); Otto Fischer and Hans Loewe, *J. prakt. Chem.*, [2] **92**, 54 (1915); G. Goldschmiedt, *Monatsh.*, **27**, 849 (1900); Émile Severin, *Compt. rend.*, **130**, 723, 1405 (1900); **142**, 1274 (1906); *Bull. soc. chim.*, [3] **23**, 374 (1900); **25**, 500 (1901).

[5] E. C. White and S. F. Acree, THIS JOURNAL, **41**, 1197 (1919).

boiling 95% ethyl alcohol to remove any adhering oil. A small amount of the compound dissolved and was recovered by concentrating the alcoholic extract. The "intermediate acid" was then purified by recrystallization from water. It is very soluble in hot water and slightly soluble in cold water. It crystallizes from water in colorless plates with two molecules of water of crystallization; yield, 55 g., 43%.

*Anal.* Subs., 1.3831, 1.4281: loss at 125°, 0.1463, 0.1512. Calcd. for $C_{15}H_{15}O_4NS + 2H_2O$: $H_2O$, 10.56. Found: $H_2O$, 10.82, 10.59. Subs., 0.3134, 0.2432: $BaSO_4$, 0.2399, 0.1863. Subs., 0.8400: cc. of 0.1 *N* $H_2SO_4$, 28.42. Calcd. for $C_{15}H_{15}O_4NS$: S, 10.51, N, 4.59. Found: S, 10.51, 10.52; N, 4.74.

Aqueous solutions of the acid change from colorless to a light greenish-yellow at $P_H$ 3.4–3.6. The color is too faint for use as an indicator. At 230–235° the substance slowly decomposes forming a green liquid.

**Barium Salt.**—Five grams of barium carbonate was added to a solution of 5 g. of the acid in 150 cc. of water which was then boiled for two hours. The excess of barium carbonate was filtered off and the filtrate concentrated to crystallization. The following analyses proved the yellow, transparent crystals which separated to be the barium salt of 4¹-dimethylaminobenzophenone-2-sulfonic acid with three molecules of water of crystallization.

*Anal.* Subs., 0.7378: $BaSO_4$, 0.2150. Subs., 1.0588: loss at 130°, 0.0716. Calcd. for $(C_{15}H_{14}O_4NS)_2Ba + 3H_2O$: Ba, 17.18; $H_2O$, 6.76. Found: Ba, 17.13; $H_2O$, 6.76. Subs., 0.9818: $BaSO_4$, 0.3090. Calcd. for $(C_{15}H_{14}O_4NS)_2Ba$: Ba, 18.42. Found: Ba, 18.50.

The barium salt is soluble in acetone, methanol, ethanol; slightly soluble in benzene, chloroform, carbon tetrachloride and insoluble in petroleum ether.

**Action of Anhydrous Ammonia.**—A sample of the dry acid was exposed to an atmosphere of dry ammonia until it was saturated. On standing in an evacuated desiccator over sulfuric acid for some time the excess ammonia was given off and the stable, yellow ammonium salt remained.

*Anal.* Subs., 1.2783: $NH_3$, 0.0768. Calcd. for $C_{15}H_{15}O_4NS + NH_3$: $NH_3$, 5.29. Found: $NH_3$, 5.67.

CONTRIBUTION FROM THE
BAKER LABORATORY OF CHEMISTRY
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FREDERICKSBURG, VIRGINIA

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**Note on α,β-Dicyclohexylethylene Glycol.**—In a paper on the maximal catalytic reduction of benzoins,[1] a compound provisionally identified as α,β-dicyclohexylethylene glycol was obtained. This compound has now been synthesized and the identification confirmed.

Attempts to condense hexahydromandelonitrile[2,3] and hexahydromandelamide[3] with cyclohexylmagnesium bromide,[4] with a view to the reduction of the resulting benzoin,[5] gave only unchanged materials. Monomolecular

[1] Buck and Ide, THIS JOURNAL, **53**, 3510 (1931).
[2] Zelinsky, *Ber.*, **41**, 2677 (1908).
[3] Godchot and Frezouls, *Compt. rend.*, **150**, 1248 (1910).
[4] Wood and Comley, *J. Soc. Chem. Ind.*, **42**, T429 (1923).
[5] Buck and Jenkins, THIS JOURNAL, **51**, 2163 (1929).

glyoxal[6] passed into a solution of cyclohexylmagnesium bromide gave a poor yield of the iso compound, iso-$\alpha,\beta$-dicyclohexylethylene glycol, a result in line with the formation of iso-hydrobenzoin by a similar method.[7]

Finally, dodecahydrobenzoin was prepared by the method of Danilow and Venus-Danilowa.[8] This compound was reduced catalytically, and gave an excellent yield of a product which proved to be identical with the previously described compound melting at 194°. Mixed melting point determinations showed no depression.

**Hexahydromandelonitrile** is a pale yellow, fairly mobile oil, with a faint aromatic odor. It is surprisingly stable and may be distilled under reduced pressure (reported undistillable by Godchot and Frezouls[3]). It is smoothly converted by the Radziscewski[9] method into the amide[3]: b. p. 104° (0.70 mm.), 121° (1.6 mm.), $d_{25}^{25}$ 1.0163, $n_D^{25}$ 1.4716, $M_D$ ($n^2$) calcd. 38.29, found, 38.19.

*Anal.* Calcd. for $C_8H_{13}ON$: C, 69.01; H, 9.42. Found: C, 68.68; H, 9.72.

**Iso-$\alpha$-$\beta$-dicyclohexylethylene Glycol.**—When recrystallized from aqueous alcohol, the compound forms a white, felted mass of slender needles. It is very soluble in absolute alcohol and in most of the usual solvents. Cold, concd. sulfuric acid gives no coloration. The melting point is 153° (corr.).

*Anal.* Calcd. for $C_{14}H_{26}O_2$: C, 74.27; H, 11.59. Found: C, 74.61; H, 11.64.

[6] Harries and Temme, *Ber.*, **40**, 165 (1907).
[7] Wren and Still, *J. Chem. Soc.*, **103**, 1772 (1913).
[8] Danilow and Venus-Danilowa, *Ber.*, **62**, 2653 (1929).
[9] Method of Rupe and Majewski, *Ber.*, **33**, 3401 (1900).

CONTRIBUTION FROM THE
EXPERIMENTAL RESEARCH LABORATORIES
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## COMMUNICATIONS TO THE EDITOR

### THE PHOTOCHEMICAL REACTION BETWEEN HYDROGEN PEROXIDE AND HYDROGEN OR CARBON MONOXIDE IN THE GAS PHASE

*Sir:*

The absorption spectrum of gaseous hydrogen peroxide has been shown by Urey, Dawsey and Rice[1] to be continuous below 3000 Å. Their interpretation of the continuum favored the direct dissociation into OH radicals, namely

$$H_2O_2 \xrightarrow{h\nu} 2OH$$

In order to test this point of view the writer carried out experiments to

[1] Urey, Dawsey and F. O. Rice, THIS JOURNAL, **51**, 1376 (1929).

detect the presence of OH radicals by a possible interaction with hydrogen molecules or carbon monoxide. If the dissociation occurs according to

$$H_2O_2 \xrightarrow{h\nu} H_2O + O$$

no interaction with hydrogen or carbon monoxide should be observed, because the oxygen atoms would be expected to react with hydrogen peroxide much faster than with hydrogen or carbon monoxide.[2]

The experiments were so carried out that a mixture containing a constant percentage of hydrogen peroxide (about 1%) and the rest hydrogen or carbon monoxide was continuously recirculated in a system at 40°. The drop in pressure represented the disappearance of hydrogen or carbon monoxide. Details of the experimental arrangement will be published later. In the case of carbon monoxide, carbon dioxide could easily be detected in a barium hydroxide solution. The gases were illuminated with the radiation 2070 Å. and 2530 Å. from a zinc spark. Blank experiments were made in the dark.

A very decided but slow reaction was measured. The following table gives a few representative experiments.

TABLE I

| Mixture | Partial pressure of $H_2O_2$ approx. in mm. | Time of illumination, min. | Total pressure Initial | Total pressure Final | Decrease in pressure per hour in mm. |
|---|---|---|---|---|---|
| $H_2O_2 + H_2$ | 5 | 70 | 712.5 | 709.6 | 2.5 |
| | 5 | 50 | 711.1 | 709.0 | 2.5 |
| $H_2O_2 + CO$ | 5 | 60 | 706.0 | 702.0 | 4.0 |
| | 2 | 60 | 702.7 | 700.4 | 2.3 |

The results may best be explained on the basis of dissociation of hydrogen peroxide into OH radicals. These then collide with hydrogen or carbon monoxide and react in the following way with a low efficiency

$$OH + H_2 = H_2O + H \quad (1)$$
$$OH + CO = CO_2 + H \quad (2)$$

Both reactions have long been proposed by Bonhoeffer and Haber.[3]

The results as they stand furnish an upper limit of the efficiency of Reactions 1 and 2. A more exact value will be given elsewhere[4] together with a discussion of its bearing on the much discussed mechanism of the chains in the thermal reaction between hydrogen and oxygen.

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RECEIVED SEPTEMBER 30, 1931
PUBLISHED FEBRUARY 5, 1932

[2] See Kistiakowsky, THIS JOURNAL, **52**, 1868 (1930), and Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931), for the reaction between O atoms and $H_2$ or CO.

[3] Bonhoeffer and Haber, *Z. physik. Chem.*, **137A**, 263 (1928). See also Lavin and Jackson, THIS JOURNAL, **53**, 383, 3189 (1931), for Reaction 2.

[4] G. von Elbe and Bernard Lewis, THIS JOURNAL, **54**, 552 (1932).

## THE COMPOSITION OF THE ATOMIC NUCLEUS

*Sir:*

In recent papers on the atomic nucleus by Harkins,[1] Latimer[2] and Urey[3] various combinations of (1) helium nuclei, (2) additional binding electrons or cementing electron pairs and (3) additional protons and electrons are used to make up the isotopic weight, *i. e.*, the *mass* of the atom. However, it seems that the atomic number, *i. e.*, the *positive charge* on the nucleus, is more significant. If this charge is due to $\alpha$-particles alone, which are after all the only nuclear fragments of appreciable mass obtained during radioactive decay, it follows that their number in the nucleus is equal to one-half the atomic number, $\alpha = AN/2$, where $\alpha$ is $p_4e_2$. If the number of protons and electrons corresponding to $AN/2$ $\alpha$-particles is subtracted from the total number of protons and electrons in the nucleus of any isotope, there remains in *every case an equal number* of protons and electrons. This leads to the conclusion that Harkins' isotopic number must be interpreted as the number of neutrons, *pe*, or a proton and an electron.[4]

The simplest groupings of protons and electrons in the nucleus is therefore as

$p_4e_2$ or $\alpha$, helium nuclei or $\alpha$-particles—the number of which is equal to one-half the atomic number

$p_2e$ or $\alpha_{0.5}$, half $\alpha$-particles—only one of these occurs in each element with odd atomic number

*pe* or *n*, neutrons—the number of which is equal to the isotopic number, that is, the proton number minus twice the atomic number. This number ranges from 0 to 54.

With this concept it is also possible to harmonize Latimer's nuclear structure by modifying the number of $\alpha$-particles to be $AN/2$ and substituting the proper number of neutrons for cementing electron pairs, thereby avoiding the difficulty of ascribing the same number of helium nuclei to different elements, and a different number of helium nuclei to the isotopes of the same element.

Isotopes differ therefore only in the number of neutrons and radioactive decay can be explained as follows

| $AN$ or $p - e$ | | Total no. of $p$ and $e$ | Composition as $\alpha$ and $n$ | Nuclear change during decay |
|---|---|---|---|---|
| 92 | U I | $p_{238}e_{146}$ | $\alpha_{46}n_{54}$ | loss of $p_4e_2$ or $\alpha$ |
| 90 | U $X_1$ | $p_{234}e_{144}$ | $\alpha_{45}n_{54}$ | loss of $e$ or $2n$ and gain of $\alpha_{0.5}$ |
| 91 | U $X_2$ | $p_{234}e_{143}$ | $\alpha_{45.5}n_{52}$ | loss of $e$ or $2n$ and gain of $\alpha_{0.5}$ |
| 92 | U II | $p_{234}e_{142}$ | $\alpha_{46}n_{50}$ | loss of $p_4e_2$ or $\alpha$ |
| 90 | Io | $p_{230}e_{140}$ | $\alpha_{45}n_{50}$ | loss of $p_4e_2$ or $\alpha$ |
| 88 | Ra | $p_{226}e_{138}$ | $\alpha_{44}n_{50}$ | |
| and so on | | | | |

[1] Harkins, *Phys. Rev.*, **38**, 1270 (1931).

[2] Latimer, THIS JOURNAL, **53**, 981 (1931).

[3] Urey, *ibid.*, **53**, 2872 (1931).

[4] Langer and Rosen, *Phys. Rev.*, **37**, 1579 (1931).

This shows that during $\beta$-decay a half $\alpha$-particle is formed from two neutrons, $2pe \longrightarrow p_2e + e$; inasmuch as two $\beta$-decays follow each other in rapid succession, the net result for the nucleus is the formation of an $\alpha$-particle, $2p_ee \longrightarrow p_4e_2$.

Artificial disintegration could then be explained by the expulsion of neutrons and this would be possible only with $Li^7$, $Be^9$, $B^{11}$, $C^{13}$, $O^{17}$ and $O^{18}$, etc., but not with Li,[6] Be,[8] B,[10] etc.

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RECEIVED OCTOBER 27, 1931
PUBLISHED FEBRUARY 5, 1932

## THE ATOMIC WEIGHTS OF SELENIUM AND OF TELLURIUM

*Sir:*

The chemically determined values for the atomic weights of selenium and of tellurium have recently been questioned by Aston[1] on the basis of improved measurements with the mass spectrograph.

With the advantage of increased precision in the measurements of relative amounts of the isotopic constituents, Aston reports the following relative percentages: for tellurium, $Te_{125}$ (6.6%), $Te_{126}$ (20.9%), $Te_{128}$ (36.1%) and $Te_{130}$ (36.4%); and for selenium, $Se_{74}$ (0.9%), $Se_{76}$ (9.5%), $Se_{77}$ (8.3%), $Se_{78}$ (24.0%), $Se_{80}$ (48.0%) and $Se_{82}$ (9.3%). Corrected for packing effects and converted to the chemical oxygen scale these figures lead to respective atomic weights $128.03 \pm 0.1$ and $78.96 \pm 0.04$. The limits of error are those assigned by Aston. The atomic weights determined by chemical means are, respectively, 127.5 and 79.2.[2] These latter values have stood for over twenty years although subjected to frequent careful redeterminations by different workers.[3] Tellurium, in particular, has received more than usual attention due to its anomalous position with respect to iodine in the older arrangements of the Periodic Table.

$Te_{125}$ is a new discovery. Its discovery, together with the discoveries of $Ba_{136}$ and $Sr_{87}$ also reported by Aston,[1] constitutes confirmation of

[1] Aston, *Proc. Roy. Soc.* (London), **A132**, 487 (1931).

[2] Table of International Atomic Weights, Report of the Committee on Atomic Weights of the International Union of Chemistry, THIS JOURNAL, **53**, 1627 (1931).

[3] Baker and Bennett, *J. Chem. Soc.*, **91**, 1849 (1907); Harcourt and Baker, *ibid.*, **99**, 1311 (1911); Marckwald and Foizik, *Ber.*, **43**, 1710 (1910); Flint, THIS JOURNAL, **34**, 1325 (1912); Dudley and Bowers, *ibid.*, **35**, 875 (1913); Dennis and Anderson, *ibid.*, **36**, 882 (1914); Staehler and Tisch, *Z. anorg. allgem. Chem.*, **98**, 1 (1916); Bruylants and Desmet, *Bull. soc. chim. Belg.*, **28**, 264 (1919); Bruylants and Michielson, *Bull. sci. acad. roy. Belg.*, [V] **5**, 119 (1919); Bruylants and Bytebier, *Bull. Belg. acad.*, 856 (1912); Kusma and Kruhlik, *Trans. Bohemian acad. of Emperor Francis Joseph*, **19**, No. 13 (1910); Jannek and J. Meyer, *Z. Electrochem.*, **19**, 833 (1913); *ibid.*, **83**, 51 (1913); Bruylants and Dondeyne, *Bull. sci. acad. roy. Belg.*, [V] **8**, 387 (1922); Bruylants, La Fortuen and Verbruggen, *Bull. soc. chim. Belg.*, **33**, 587 (1924 .

definite predictions which were recently made by the writer.[4] The further discoveries by Aston of $Ba_{135}$ and $Ba_{137}$ are also concordant with these predictions. Further predictions of isotopes whose discoveries have not yet been reported include three additional tellurium isotopes, $Te_{120}$, $Te_{122}$ and $Te_{124}$, with the possibility of $Te_{123}$ as well, and two additional selenium isotopes, $Se_{79}$ and $Se_{81}$. It is significant that allowance for these additional isotopes will change Aston's computed values in the directions of the chemical atomic weights, both for selenium and for tellurium.

Small uncertainties which, of course, do exist in the chemical atomic weights preclude the possibility of an exact estimate of the proportions in which these additional isotopes exist. However, we expect that these uncertainties are small compared with the divergences between the chemical and the mass spectrograph values. Hence we can make predictions as to the approximate percentages of these isotopes. These predictions lead to about 8% of $Te_{120}$, $Te_{122}$, $Te_{124}$ (and possibly $Te_{123}$), taken collectively, and to about 9% of $Se_{81}$. No estimate for the amount of $Se_{79}$ is possible. Failure heretofore to observe the 8% mixture of tellurium isotopes is reasonable since the 6% of $Te_{125}$ alone remained, until now, undiscovered. Proximity to the very abundant $Se_{80}$ (48%) may account for failure to observe both $Se_{81}$ and $Se_{79}$.

The writer's predictions of these isotopes, as of $Te_{125}$, $Ba_{136}$ and $Sr_{87}$, were based on the positions of missing atoms in a "Periodic Table" of atomic nuclei.[4] Independently, Professor H. C. Urey[5] made similar predictions, including isotopes of selenium and of tellurium. The predictions of further missing isotopes can now be extended to include $Ce_{141}$, $Ce_{144}$, and $Nd_{148}$. As a convenient aid in using the "Periodic Table" of isotopes it is useful to observe that the positions at which the various isotopes of a given element may occur occupy a pattern similar to successive knight moves on a chess board.

[4] Johnston, THIS JOURNAL, **53**, 2866 (1931).
[5] Urey, THIS JOURNAL, **53**, 2872 (1931).

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RECEIVED DECEMBER 10, 1931
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## PREPARATION OF PINACOLONE

*Sir:*

Because of the need of large amounts of pinacolone for investigations in progress in this Laboratory, methods for its preparation have been studied. The usual method ["Organic Syntheses," Vol. I, pp. 87, 91] is time consuming.

We find that the addition of a dilute ether solution of tertiary-butyl-

magnesium chloride to an excess of acetyl chloride in ether gives a 40% yield of pinacolone, b. p. 103–106° at 746 mm. pressure.

Somewhat lower yields are obtained with other combinations of tertiary Grignard reagents and acyl halides.

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RECEIVED DECEMBER 26, 1931
PUBLISHED FEBRUARY 5, 1932

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## PREPARATION OF SUBSTITUTED FLUORENONES

*Sir:*

The appearance of a paper by Langecker [*J. prakt. Chem.*, [2] **132**, 145–52 (1931)] citing certain attempts to prepare 1,8-dinitrofluorenone leads us to call attention to work of a similar nature which has for some time been in progress in this Laboratory. In May, 1927, Moore and Huntress [THIS JOURNAL, **49**, 1324–1334 (1927)] published a synthesis for both 2-nitro- and for 7-nitrophenanthridone. In November of the same year it was further shown [Moore and Huntress, *ibid.*, **49**, 2618–2624 (1927)] that 7-nitrophenanthridone could be prepared in almost quantitative yield by Beckmann rearrangement of 2-nitrofluorenone oxime. In pursuance of the studies of the phenanthridone series begun at that time, the present authors have been engaged since 1927 in attempting to obtain derivatives of fluorenone having substituents in one (or both) of the 1,8 positions. If an unsymmetrically substituted fluorenone oxime of this type could be obtained, it was hoped that stereoisomers might be isolated, and that by joint application of phenanthridone formation and of ring closure reactions involving the substituent and the oximino group, some additional light might be thrown upon the mode of interchange of radicals in the Beckmann rearrangement. Since Langecker's paper indicates its objective as the preparation of 1-substituted fluorenones, and since in dealing with the 2-nitrofluorenone oxime first reported by one of us it gives no evidence that the author was aware of our previous publications on fluorenone derivatives, it seems advisable that we reiterate the continuing interest of this Laboratory in this subject.

Of the few 1- or 1,8-substituted fluorenones on record in the literature (1-bromofluorenone, 1,3-dibromofluorenone, 1-hydroxyfluorenone, 1-aminofluorenone, fluorenone-1,7-dicarboxylic acid, and 1,8-dinitrofluorenone), the alleged "1,8-dinitrofluorenone" of Schmidt and Stützel [*Ann.*, **370**, 22 (1909)] and of Kuhn and Jacob [*Ber.*, **58**, 1440 (1925)] is the only substance prepared by direct substitution. The structure assigned to this material is open to criticism upon several grounds. In the first place the nitrogen content given by Schmidt as 10.40% proves upon recalculation

of Schmidt's own experimental data to be in fact 8.08%, or about half-way between the theoretical value of 6.22% for a mononitrofluorenone and 10.36% for a dinitrofluorenone. In the second place, oxidation of the material yielded an acidic product whose observed melting point and nitrogen analysis suggested that it might be *o*-nitrobenzoic acid. Despite the proximity of the melting points of *o*- and of *m*-nitrobenzoic acids, no other derivatives of this oxidation product were prepared. Assuming for the moment that the product really was *o*-nitrobenzoic acid, the result accounts for only one of the nitro-substituted nuclei and does not necessarily imply that the same position in the other was involved. The supposed existence of stereoisomeric dinitrobenzidines and dinitrotolidines was based upon negative evidence of this kind. In the third place recent developments have shown that directly contrary to the assumptions prevalent at the time of Schmidt and Stützel's publication there is a strong tendency toward unsymmetrical nitration in the biphenyl series, in the phenanthraquinone series, and in the fluorene series.

In pursuance of our desire to obtain an appropriately substituted fluorenone oxime, we attempted to repeat the work of Schmidt and Stützel. In no case, however, was any material obtained possessing the properties ascribed to "1,8-dinitrofluorenone." In four separate experiments using Schmidt's conditions we obtained instead a 70% yield of 2-nitrofluorenone. The identity of this substance was established in four ways: (1) by analysis for nitrogen; (2) by its melting point and its failure to depress the melting point of a sample of authentic 2-nitrofluorenone; (3) by the identity of its phenylhydrazone with that of authentic 2-nitrofluorenone as shown by comparison and by mixed melting point determinations; and (4) by its reduction to 2-aminofluorenone. We can confirm Langecker, therefore, in stating that nitration of 9-acetylaminofluorene by the method of Schmidt and Stützel gives 2-nitrofluorenone as the only tangible product.

In examining the effect of varying the stated conditions, we have observed that when 9-acetylaminofluorene is treated with concentrated nitric acid (*d* 1.42) for two hours at 100° there results a mixture from which we have isolated a 30% yield of 2,7-dinitrofluorenone, together with 13% of a new dinitrofluorenone, m. p. 213–4° uncorr. This substance contains 10.57% of nitrogen as compared with the theoretical of 10.60% for a dinitrofluorenone. It depressed the melting points of both 2,7-dinitro- and 2,4-dinitrofluorenones. Its structure is being examined.

The melting point of Langecker's 2-nitrofluorenone oxime is given as 249°. Moore and Huntress [THIS JOURNAL, **49**, 2622 (1927)] obtained a value of 262.5–263.0° uncorr., with decomposition. Since the former material was prepared from the ketone by means of hydroxylamine hydrochloride and barium carbonate in alcohol (*i. e.*, in neutral solution) while our product was prepared from hydroxylamine hydrochloride and an

alcoholic solution of the ketone (*i. e.*, in acid solution), it is possible that the two materials are stereoisomers. This point will be examined.

Our efforts to prepare fluorenones substituted in positions ortho to the carbonyl group are being continued.

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RECEIVED DECEMBER 28, 1931
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## REACTION OF PHENYLACETONITRILE

*Sir:*

While investigating the action of sodium on benzyl cyanide, it was found that one mole of phenylacetonitrile dissolved in liquid ammonia reacts almost quantitatively with one mole of sodium to form a salt, presumably sodium phenylacetonitrile, which remains suspended in liquid ammonia. This when treated with ethyl bromide in liquid ammonia yields phenylethylacetonitrile.

In previous work Rossolymo used sodium hydroxide, Hintikka, sodamide in toluene, Bodroux and Taboury, sodamide in ether, Rising, sodium in ether, Rising and Zee, sodamide in ether, as a means of forming sodium phenylacetonitrile.

It is interesting to note that presumably only one of the hydrogen atoms on the carbon atom, alpha to the cyanide group, can be replaced at one time by sodium in liquid ammonia. If, after treatment with ethyl bromide to form phenylethylacetonitrile, this latter nitrile is treated with sodium in liquid ammonia, a mole of sodium can be introduced per mole of nitrile.

This procedure can be utilized in the preparation of mono and dialkylated alkyl or aryl cyanides. It is being investigated further in these laboratories.

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PUBLISHED FEBRUARY 5, 1932

## THE CRYSTALLINITY OF OPALS AND THE EXISTENCE OF HIGH-TEMPERATURE CRISTOBALITE AT ROOM TEMPERATURE

*Sir:*

Opals have thus far been considered as outstanding examples of truly amorphous solids. The introduction of x-ray methods did not alter this result materially since Lehmann [W. M. Lehmann, *Z. Krist.*, **59**, 455 (1923)] reported that gem opal and ordinary opal give the Debye–Scherrer–Hull diagram of an amorphous solid; however, fire opal gives a faint in-

dication of crystallinity. Later Rinne [F. Rinne, *Z. Krist.*, **60**, 55 (1924)] studied several samples of opals by means of x-rays and found them to be amorphous.

The results obtained in this Laboratory are quite different from these previous findings. Thus far fifteen samples of various types of opal have been investigated, all of which show definite crystallinity which is very pronounced in the majority of the cases. Also most of the samples give an identical pattern.

This pattern is of unusual interest since it does not correspond to either low-quartz, low-tridymite or low-cristobalite, which are the only modifications of silica ever definitely established to exist at room temperature.

The pattern, is however, in perfect agreement with the one of high-temperature cristobalite as reported by Wyckoff [R. W. G. Wyckoff, *Am. J. Sci.*, **9**, 448 (1925)., *Z. Krist.*, **62**, 189 (1925)].

Comparison with a picture of the cubic high-temperature form prepared in this Laboratory confirms this identity. The unlikely possibility of a hydrate of similar structure is excluded by the fact that the diagram remains unchanged after heating of the sample for one hour at 1100°.

Two reports have been made suggesting that high temperature cristobalite might persist at room temperature for some time, but according to Sosman [R. B. Sosman, "The Properties of Silica," The Chemical Catalog Co., Inc., New York, 1927, p. 133] these claims, based on optical examination, are of doubtful validity; 200° is the lowest temperature at which high-cristobalite has been observed to exist according to reliable experiments (compare Sosman).

However, we have now provided definite proof of the existence of high-temperature cristobalite at room temperature for an indefinite period of time.

These investigations are being continued and a complete report will appear soon.

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ISADOR LEVIN
EMIL OTT

RECEIVED JANUARY 2, 1932
PUBLISHED FEBRUARY 5, 1932

## THE STARCH-IODIDE REACTION

*Sir:*

Remington, McClendon and von Kolnitz have recently reported [THIS JOURNAL, **53**, 1245 (1931)] that they could not confirm Turner's observations as to the reliability and stability of the color produced by the starch–iodide reaction. They state that 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 the time. These

conclusions were drawn apparently from a study of four standard solutions each containing 0.001 mg. of iodine. Their figures show an error of over 100% as read in the colorimeter against their blue glass.

Three years of careful study with the starch–iodide test indicate that the standard solutions prepared as described by Turner are reliable, stable and sufficiently uniform for clinical estimation of small amounts of iodine.

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RECEIVED JANUARY 2, 1932
PUBLISHED FEBRUARY 5, 1932

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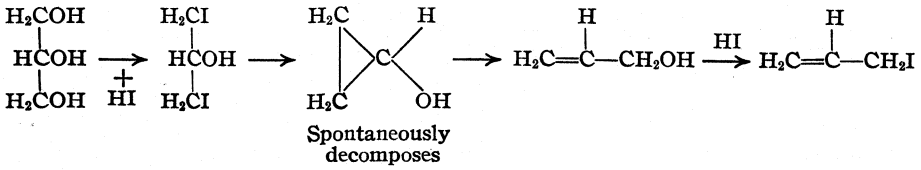
## THE ACTION OF HYDRIODIC ACID ON GLYCEROL

*Sir:*

The following seems reasonably good evidence for the mechanism involved in the formation of allyl iodide in the well-known reaction between glycerol and hydriodic acid.

When $CH_2Br\text{-}CH_2\text{-}CH_2Br$ is treated with zinc or sodium, cyclopropane is formed. However, when $CH_2Br\text{-}CHOH\text{-}CH_2Br$ [Aschan, *Ber.*, **23**, 1833 (1890)] or $CH_2Cl\text{-}CHOH\text{-}CH_2Cl$ is similarly treated [Hübner and Müller, *Ann.*, **159**, 168 (1871); Tornöe, *Ber.*, **24**, 2674 (1891)] allyl alcohol is formed and not cyclopropanol. Strange as it may seem, $CH_2Br\text{-}CHOOR\text{-}CH_2Br$ in absolute ether yields with sodium not cyclopropyl benzoate or acetate but allyl benzoate and allyl acetate, depending, of course, on the nature of the group R. Furthermore, in the action of nitrous acid on cyclopropyl amine, allyl alcohol is formed [Kishner, *Chem. Zentr.*, I, 1704 (1905)] and not cyclopropanol, while in the electrolysis of the potassium salt of cyclopropane monocarboxylic acid, the allyl ester of cyclopropane monocarboxylic acid was obtained [Fichter and Reeb, *Helv. Chim. Acta*, **6**, 454 (1923); Hofer and Moest, *Ann.*, **323**, 284 (1902)] and not the cyclopropyl ester of the cyclopropane monocarboxylic acid. Furthermore, allyl alcohol was obtained from diiodohydrin [Claus, *Ann.* **168**, 28 (1873); Swarts, *Z. Chem.*, 255 (1868)] when that compound was merely allowed to stand. The unstable nature of cyclopropanol offers a clue to the action of hydriodic acid on glycerol. In the light of the foregoing reactions, the following may be postulated



Experiments are under way in this Laboratory to test further the instability of hydroxycyclopropane derivatives.

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LOUIS SATTLER

RECEIVED JANUARY 7, 1932
PUBLISHED FEBRUARY 5, 1932

## PYRIMIDINE AZO DERIVATIVES

*Sir:*

There has just come to our attention the article by Johnson, Baudisch and Hoffman, entitled "Ueber die Bildung von Diazo-uracilanhydrid aus Amino-uracil" ("Concerning the Formation of Diazo-uracilanhydrid from Amino-uracil") in the November, 1931, number of the *Berichte* [*Ber.*, **64**, 2629–2631 (1931)]. Since this article is entitled a "Vorläufige Mitteilung (Preliminary Communication)" and concludes with the sentence "Die Versuche sollen fortgesetzt werden (The experiments are to be continued)," it seems desirable, for the sake of avoiding, so far as may be possible, overlapping of work and duplication of effort, for us to report that prior to the appearance of this article in the *Berichte* we had already completed an investigation of five different types of pyrimidine azo derivatives, and that an article covering this research will appear shortly.

Our studies have included the following groups of reactions: (1) the coupling of aromatic diazonium salts with hydroxypyrimidines; (2) the coupling of diazopyrimidines with aromatic phenols and amines; (3) the coupling of diazopyrimidines with hydroxypyrimidines; (4) the condensation of hydroxypyrimidines with hydrazines, and (5) the condensation of hydrazinopyrimidines with hydroxypyrimidines.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.
MARSTON T. BOGERT
DAVID DAVIDSON

RECEIVED JANUARY 14, 1932
PUBLISHED FEBRUARY 5, 1932

## DILUTE HYDROCHLORIC ACID SOLUTIONS AND THE DEBYE–HÜCKEL THEORY

*Sir:*

Whether the Debye–Hückel theory is in entire quantitative agreement with the facts even for dilute 1:1 aqueous strong electrolytes at ordinary temperatures is a question which is not yet regarded as closed by all investigators. This is clearly shown in the recent review by Lange and Streeck [*Z. Elektrochem.*, **37**, 698 (1931)]. Davies, in "The Conductivity of Solutions," New York, 1930 and elsewhere has repeatedly expressed the view, supported by some evidence, that in the case of monobasic acids

the limiting value of the ratio of $-\log f$ to $c^{1/2}$ is not 0.5 as required by the theory but something nearer to 0.38.

Since both Davies and Lange and Streeck discuss hydrochloric acid, and conclude that in this case the data are inadequate to decide the question, new evidence on this substance should be particularly welcome. Using the value of $E°$ given by Carmody in his recent paper [THIS JOURNAL, **54**, 188 (1932)] a simple calculation yields as values of the ratio of $-\log \gamma$ to $m^{1/2}$: 0.47, 0.45, 0.43, 0.45, 0.47, 0.47 and 0.47 for the seven lowest molalities studied by Carmody, ranging from 0.005 to 0.0003 molal. The mean value 0.46 is slightly lower than the Debye–Hückel value, as has been noted in many other cases, but is not inconsistent with it in view of the experimental uncertainty of the e. m. f. measurements. Carmody's careful investigation certainly lends no support to Davies' views.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
NORRIS F. HALL

RECEIVED JANUARY 18, 1932
PUBLISHED FEBRUARY 5, 1932

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## OXYACIDS OF FLUORINE

*Sir:*

When fluorine is passed into a 50% solution of potassium hydroxide cooled to $-20°$, potassium fluoride separates and the supernatant liquid actively liberates iodine from a solution of potassium iodide. This liquid maintains its oxidizing power for several days at room temperature, even after air has been passed through it for some time, and even after being heated for three hours at 60°. These results seem to preclude the possibility of the oxidation being due to ozone.

To test this point still further, ozone was passed through a cold solution of lithium hydroxide for a considerable time. The liquid showed no oxidizing power. When, however, fluorine was passed into a solution of lithium hydroxide under identical conditions, the resulting liquid was strongly oxidizing, and when this solution was evaporated to dryness on a water-bath and the residue was dissolved in water, the solution still showed strong oxidizing power.

Similarly, a solution of calcium hydroxide was found to be unaffected by ozone, but to have a marked oxidizing action after treatment with fluorine.

These alkaline solutions retained their oxidizing character even after acidification with sulfuric acid, which indicated the presence of an oxyacid of fluorine.

To prepare a solution of the free oxyacids, fluorine was passed into a suspension of calcium carbonate in cold water, and the contents of the

flask was then subjected to distillation. The distillate had an acid reaction and actively oxidized a neutral solution of potassium iodide.

Approximate determinations of the ratio of hydrogen to oxygen in the distillate from three separate distillations gave 1:2.31, 1:2.22 and 1:2.80. These results indicate the presence of fluoric acid ($HFO_3$) in the distillate; and a greater oxidizing power of the liquid in the reaction flask, before distillation from the calcium carbonate, indicates that a less stable oxy-acid of fluorine, probably hypofluorous acid (HFO), is also formed. It may here be added that the distillate contained no trace of chlorine.

When fluorine was passed into a cold solution of cesium carbonate until the salt had been entirely converted into fluorine compounds, the resulting liquid was extremely reactive. It was evaporated to dryness on a water-bath, and a water solution of the residue showed strong oxidizing power. Fractional solution of this residue with successive small amounts of water indicated that the oxidizing power is greatest in the most soluble portions.

This investigation is being carried forward and detailed results will be published later.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

L. M. DENNIS
E. G. ROCHOW

RECEIVED JANUARY 22, 1932
PUBLISHED FEBRUARY 5, 1932

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## THE THERMAL DISSOCIATION OF NITROUS OXIDE

*Sir:*

From the known entropies of other triatomic molecules it is possible to determine a value for the entropy of nitrous oxide which is probably correct within a few entropy units. Following the procedure used in a recent article by the author [THIS JOURNAL, **54**, 156 (1932)] the value $S^{\circ}_{298}$ $(N_2O)g$ = 51.9 E. U. is obtained. This leads to interesting conclusions regarding the thermal dissociation of nitrous oxide into nitrogen molecule and oxygen atom, for the entropy change in this reaction can now be determined, and the change in heat content is known. Thus the free energy change at 298°K. can be found, and by the use of empirical specific heat equations a good estimate of the free energy change at 838°K. can be made and thus of the equilibrium constant $K = p_{N_2} \cdot p_O / p_{N_2O}$. An approximate value such as this is quite sufficient to show that the equilibrium pressure of oxygen atoms is surprisingly high, being of the order of $10^{-4}$ atm. at this temperature.

At 838°K. the thermal rate of decomposition is low. For the purposes of a calculation to be made in a moment, let us consider simply as an example the thermal rate in a bulb at this temperature containing 190 mm. of $N_2O$ and 10 mm. of $N_2$. The rate of decomposition is of the order of

$10^{13}$ molecules per cc. per sec. [Hinshelwood and Burk, *Proc. Roy. Soc.* (London), **A106,** 284 (1924)]. On the other hand, the number of collisions between $N_2O$ molecules and oxygen atoms at the equilibrium concentration under these conditions proves to be of the order of $10^{24}$ collisions per cc. per sec., and thus the thermal decomposition is very small compared to this. We are thus forced to the conclusion that either the probability of reaction between $N_2O$ and O is very small, or that the rate of thermal dissociation into $N_2$ and O is very small, never even approximately establishing equilibrium even for low rates of the thermal decomposition. Both statements may, of course, be true. The first is not at all surprising, rather, indeed, probable. However, the second statement, also, may very possibly be true. In this case, in contrast to the case of ozone (see first reference cited above), we are dealing with a molecule made up of the dissociation products O (normal state $^3P$) and $N_2$ (normal state $^1\Sigma$) and this, in addition to all chemical knowledge of the inertness of nitrogen, suggests that the two reactions represented by the equilibrium $N_2O \rightleftharpoons N_2 + O$, even at 838°K., are very slow. In the case of the molecule $O_3$ the situation is different, the constituents being O (normal state $^3P$) and $O_2$ (normal state $^3\Sigma$). It should be noted that, with respect to the dissociation products, the energy content of the two molecules $N_2O$ and $O_3$ is of the same order of magnitude, namely, about 41,500 calories and 24,000 calories, respectively. The author plans to discuss the above more fully in a later paper.

BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
OLIVER R. WULF

RECEIVED JANUARY 26, 1932
PUBLISHED FEBRUARY 5, 1932

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## THE STRUCTURE OF METAL KETYLS

*Sir:*

The metal ketyl derived from benzophenone has been found to conduct the electric current in liquid ammonia solution [observations of Mr. Paul B. Bien in this Laboratory] and the results also suggest that this substance is ionized in accordance with the equation

$$(C_6H_5)_2CONa \longrightarrow [(C_6H_5)_2CO]^- + Na^+$$

The anion represents an interesting and unusual type of stable complex for it contains both an *odd* and an *extra* electron. Consequently, a careful study of such substances might be expected to throw some new light on fundamental valence problems.

It has already been shown [Wooster, THIS JOURNAL, **51,** 1856 (1929)] that the Schmidlin formula for the metal ketyls is incorrect and that the question of their constitution is still open. Several alternative hypotheses

including those of Schlenk and his co-workers [Schlenk and Weickel, *Ber.*, **44**, 1182 (1911); Schlenk and Thal, *ibid.*, **46**, 2840 (1913)] are now being critically studied.

CHEMICAL LABORATORY OF BROWN UNIVERSITY CHARLES BUSHNELL WOOSTER
PROVIDENCE, RHODE ISLAND

RECEIVED JANUARY 23, 1932
PUBLISHED FEBRUARY 5, 1932

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## NEW BOOKS

**An Introduction to Chemistry. A Pandemic Text.** By JOHN ARREND TIMM, Assistant Professor of Chemistry, Yale University. With a Foreword by John Johnston. McGraw-Hill Book Company, 370 Seventh Avenue, New York, 1930. xviii + 561 pp. 161 figs. 14.5 × 21 cm. Price, $3.50.

Those who are seeking something different in the way of presenting first-year chemistry will be interested in this book. It is an outgrowth of a course given at Yale for those students who desire to broaden their educational horizon by the acquisition not only of some of the pertinent facts of science but an understanding of some of the modern theories of chemistry and physics. It is not intended for those students who plan to take further training in the subject. The author has well stated in his Introduction that "A well-balanced life results from the cultivation of all of its moods. The risks of living too exclusively in any one of them are too great for any but the genius to take. In education none of these moods should be neglected. The student who studies literature and the humanities exclusively, is as ill-cultured as he who cares for science alone." And, further (from the Foreword by John Johnston), "This course endeavors, not to give the student a contemporary command of assorted facts relating to restricted classes of substances, but to correlate, and to explain in simpler terms, some of the chemical and physical phenomena which he encounters every day."

To those orthodox teachers who have always regarded chemistry essentially as a laboratory science, the idea of giving a year's course in introductory chemistry without laboratory work, without the practice of writing equations ("a cruel waste of time"), and without the working of problems, will come somewhat as a jolt. The author is certainly to be commended for his boldness in breaking away from all tradition. In choice of material, its arrangement and method of presentation, the author has thrown aside all that is conventional and, it must be admitted, has produced a book that is both informative and interesting.

The reviewer believes that if the lower seventy-five per cent. of the class of students who will desire to take a "pandemic" course in chemistry could be eliminated this would be a most excellent text. It is difficult for

him to believe that, in the hands of the average teacher, this book will be suitable for the "mine run" of students—students who are not primarily interested in chemistry and who, in general, are likely to have aptitudes for science which are below the norm for chemistry students. It may be that in the hands of the author and with a selected group of students this text with its relatively large amount of advanced material can be used with success, but the reviewer feels that for the average college freshman this text will prove to be a very heavy diet. Upper class students who have had an introductory course in chemistry in the high school followed by a course in physics in college could undoubtedly assimilate the material under the guidance of an inspirational teacher. The reviewer believes that the giving of such courses to selected groups should be encouraged. The larger universities are in a position to do this effectively. It is unfortunate that most of our curricula are devised for the *average* student and that the superior student is not encouraged to put forth his best effort. The book is one which every teacher of introductory chemistry should own—and use, for in it he will find much that is helpful.

J. H. MATHEWS

**Physics of the Earth. IV. The Age of the Earth.** By the Subsidiary Committee on the Age of the Earth. Division of Physical Sciences with the Coöperation of the Division of Geology and Geography and American Geophysical Union, National Research Council. Bulletin of the National Research Council, June, 1931, Number 80. Published by the National Research Council of the National Academy of Sciences, Washington, D. C., 1931. v + 487 pp. 17 × 25 cm. Price, paper, $4.50; cloth, $5.00.

In this book there have been brought together in one volume for the first time the essential data upon which are based the various methods for estimating the age of the earth's crystal rocks. It is much more than a mere compilation, however. The book consists of five parts, each the work of an outstanding specialist who alone has been responsible for his particular part. The contributing authors have evidently devoted much time and labor to the production of admirably comprehensive and critical reviews of the present status of their special subjects. Copious abstracts, references and bibliographies are given, rendering the book invaluable as a reference work.

Part I on "The Age of the Earth on the Basis of Sediments and Life" has been written by Charles Schuchert, who has made a most exhaustive examination and revision of the data bearing on the thickness of sediments and their rate of deposition with the result that the new age figures for this classic geological method are now more in harmony with those derived from the radioactive method. Professor Schuchert concurs with the general opinion as to the uselessness of the biological or palaeonto-

logical method based on estimates of the length of time supposedly required for the evolution of various living organisms.

Part II on "The Age of the Ocean" by Adolph Knopf shows conclusively that the method based on sodium accumulation in the ocean cannot be expected to yield reliable results.

In Part III on the "Age of Minerals from Radioactivity" Alois F. Kovarik presents a very complete and valuable new mathematical treatment of the problem of calculating the age of radioactive minerals and a "Critique of the Values of the Disintegration Constants."

Part IV, "Radioactivity and Geological Time," by Arthur Holmes, constitutes the largest and most important part of the book as a consequence of the preëminence of this method and the immense related literature already in existence. Professor Holmes, evidently at the cost of tremendous labor, has produced what must be generally admitted to be the most comprehensive, stimulating and useful work on the subject to date.

Part V, "The Age of the Earth from Astronomical Data," by Ernest W. Brown, deals with the astronomical data which have a bearing on the age of the earth.

A six-page summary by Professor Knopf of the main conclusions arrived at throughout the book is a valuable feature which will be of general interest.

The book has been written, it is stated, "to give to the reader, presumably a scientist, but not a specialist in the subject, an idea of its present status together with a forward-looking summary of its outstanding problems." This purpose has been more than fulfilled. The book will be indispensable to workers in this field.

H. V. ELLSWORTH

**Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.)** Edited by R. J. MEYER. Eighth edition. **Strontium.** System—number 29. Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1931. xxx + 239 pp. 26 figs. 17 × 25 cm. Price, to subscribers, Mk. 36; singly, Mk. 41.

This volume follows the lines of the earlier instalments of this invaluable handbook. Since strontium is number 29 in the numerical system of presentation here followed, this volume covers the element itself and its compounds with all the non-metals and many of the metals, in other words, practically all of the chemistry of strontium.

The only subject that I noticed to be missing was statistics as to the production, consumption and uses of strontium and its compounds.

The book is the joint achievement of some seven collaborators and the literature has been covered up to August 1, 1931.

ARTHUR B. LAMB

**An Introduction to the Principles of Physical Chemistry.** By O. MAASS, Professor of Physical Chemistry, and E. W. R. STEACIE, Assistant Professor of Chemistry, McGill University. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1931. vii + 269 pp. 62 figs. 15.5 × 23.5 cm. Price, $2.75.

This book is intended for students who have had elementary courses in chemistry, physics and mathematics but who have not had calculus. It embodies material given in a course of about fifty lectures at McGill University for students intending to make chemistry their profession, chemical engineers as well as pre-medical and biology students. Whether it is wise to follow a thorough freshman chemistry course by a course in physical chemistry not using any calculus at all is an open question, although the authors feel that "This makes possible a better appreciation of more advanced and detailed courses in physical chemistry, since the student thus has several years in which to assimilate the fundamental ideas."

If one grants the authors' contention that a course of this type is desirable, one must be prepared to admit that the book is exceedingly well adapted to its purpose. The real difficulty lies in the fact that the complete avoidance of even the simplest differentials and integrals necessarily leads to a highly qualitative treatment of certain matters which could be given easily in a rigorous fashion and to the introduction of formulas for which the student cannot hope to understand the origin. Thus the connection between simple reaction rate equations and their integrated forms must remain obscure to the student who knows nothing of integration. Other examples could be cited. It is perfectly true, however, that all elementary courses in physical chemistry must encounter this difficulty to a greater or less extent whether or not calculus is required as a prerequisite.

The introductory chapter contains an excellent discussion of the objects and limitations of science, the scientific method, half truths and inexact laws, the empirical and mechanistic points of view, etc. This chapter is well worth reading and many of the statements made in it are all too little appreciated by the average scientific worker.

The remaining chapters treat most of the subjects which are ordinarily included in an elementary course in physical chemistry.

Even if it is granted that there is some tendency to neglect the so-called old fashioned physical chemistry and introduce too much discussion of new developments, one feels that the present book might well have contained more reference to new points of view. For example, one finds only a brief reference to current views concerning strong electrolytes, but their degrees of dissociation as determined by conductivity and freezing point methods are used in most of the discussion. The student might get the impression that the simple ideas advanced in the early days of the ionic theory are perfectly all right for dilute solutions. Later when the aberra-

tions from Ostwald's Dilution Law are discussed one would begin to realize that something is wrong somewhere. It would seem that even without any mathematics one could introduce more of the point of view of modern physical chemistry in this respect. The entire treatment of the origin of the electromotive force at metal–solution interfaces seems to be based on the idea that one can determine the difference in charge between a single electrode and a solution. A more rigorous treatment of the subject of cells might have been given.

The phase rule is not mentioned as such and the discussion of heterogeneous equilibrium is very brief. The chapter on velocity of chemical reactions is very brief and lacks in rigor in certain places.

No mention is made at any place of such things as atomic structure, radioactivity, photochemistry and isotopes. Such omissions are probably not serious in the type of course for which the book was written.

In spite of the absence of mathematics and the consequent introduction of some things which the student will have to unlearn at a later date, the book is, on the whole, very clearly and precisely written. The general style is good and the elementary student will be sure to acquire a vivid appreciation of the reasoning which underlies the general subject. The authors have succeeded admirably in attaining the aims which prompted them to write the book.

W. ALBERT NOYES, JR.

**The Structure of Line Spectra.** By LINUS PAULING, Ph.D., and SAMUEL GOUDSMIT, Ph.D. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1930. x + 263 pp. 14.5 × 23 cm. Price, $3.50.

Although written primarily as a text for spectroscopists, this book should find a much wider field of application, since a detailed knowledge of energy levels and spectroscopic term values is becoming of increasing importance to chemists. After a brief introductory treatment of atomic theories, the authors proceed to a detailed development of the theory of line spectra, which occupies the greater part of the book. The Periodic System is discussed from the spectroscopic viewpoint and the concluding chapters deal briefly with x-ray spectra, nuclear moments and the theoretical work on the paramagnetism of ions.

The treatment is thorough throughout and as such will be more useful to those wishing a working knowledge of the subject rather than to the general reader. Experimental results are included only to illustrate the theory, no attempt having been made to give a complete summary of available data. The value of the book is best shown by the fact that it has already become the standard text on its subject.

HUGH M. SMALLWOOD

# BOOKS RECEIVED

December 15, 1931–January 15, 1932

WILLIAM CLAYTON. "Colloid Aspects of Food Chemistry and Technology." P. Blakiston's Son and Co., Inc., 1012 Walnut St., Philadelphia, Pa. 671 pp. $8.00.

R. ADAMS DUTCHER AND DENNIS E. HALEY. "Introduction to Agricultural Biochemistry." John Wiley and Sons, Inc., 440 Fourth Ave., New York. 484 pp. $4.50.

WILHELM EITEL, MARCELLO PIRANI AND KARL SCHEEL, Editors. "Glastechnische Tabellen. Physikalische und chemische Konstanten der Gläser." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 714 pp. RM. 145; RM. 149.80, bound.

RICHARD FLEISCHER AND HORST TEICHMANN. "Die lichtelektrische Zelle und ihre Herstellung." Introduction by H. Dember. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 175 pp. RM. 12; bound, RM. 13.20.

WALTER FUCHS. "Die Chemie der Kohle." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 510 pp. RM. 45.

T. MARTIN LOWRY. "Inorganic Chemistry." Second edition. The Macmillan Company, 60 Fifth Ave., New York. 1101 pp. $8.40.

JAMES WILLIAM MCBAIN. "The Sorption of Gases and Vapors by Solids." George Routledge and Sons, Ltd., 68–74 Carter Lane, E. C., London, England. 577 pp. 25 s., net.

W. WALTER MEISSNER. "Chemischer Handatlas. Anorganische Chemie unter besonderer Berücksichtigung von Atomphysik und Atomchemie." Georg Westermann Verlagsbuchhandlung, Braunschweig, Germany. 77 pp. RM. 38.

WILLY SCHMITT. "Kolloidreaktionen der Rückenmarkflüssigkeit (Technik, Klinik und Theorie)." Verlagsbuchhandlung Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 181 pp. RM. 12.50; bound, RM. 13.50.

GEORG-MARIA SCHWAB. "Katalyse vom Standpunkt der chemischen Kinetik." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 249 pp. RM. 18.60; bound, RM. 19.80.

H. ZEISE. "Reportorium der physikalischen Chemie." Der Verlag von B. G. Teubner, Leipzig, Germany. 215 pp. RM. 8.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY]


## THE NATURE OF "ALUMINUM OXIDE" HYDROSOLS


BY ARTHUR W. THOMAS AND AN PANG TAI



RECEIVED JUNE 20, 1931 PUBLISHED MARCH 5, 1932


In a previous publication, Thomas and Whitehead[1] suggested that the dispersed phase of hydrosols arising from the peptization of hydrous aluminum oxide by hydrochloric acid consists of olated and possibly oxolated aluminum oxychloride complexes. In the present communication certain properties of "aluminum oxide" hydrosols, particularly aluminum oxyiodide hydrosols, are described, showing the influence of the nature of the crystalloid "contra-ion," previous history of the hydrosols, etc., which are interpreted in the light of the proposed suggestion of their constitution.

**Preparation of Hydrosols.**—All sols were prepared by the aluminum amalgam method. A piece of pure aluminum[2] of about 350 g. was covered with slightly acidulated water and placed in contact with 10 g. of pure mercury. After three to four hours, the mercury had spread over the whole surface of the aluminum.[3] The excess of mercury was poured off and the amalgamated aluminum was rinsed with distilled water. For the preparation of the "-oxyiodide" sols it was then placed in 3 or 4 liters of distilled water and 20 to 100 cc. of 0.5 *N* hydriodic acid was added. The reaction was allowed to continue for eight hours at boiling temperature, or for one to three days at room temperature. At the end of the reaction, there was always a large amount of precipitate of alumina hydrate left on the bottom of the vessel.

The supernatant turbid solution was then poured into a flask and allowed to settle. After two days, it was centrifuged for one hour at a speed of 1200 r. p. m., rotating diameter being 42 cm. The supernatant portion was siphoned into and kept in "Non-Sol" glass bottles.

Some of the sols prepared in this way were dialyzed in nitrocellulose bags against distilled water at room temperature for four to fourteen days, the water being changed daily.

[1] Thomas and Whitehead, *J. Phys. Chem.*, **35**, 27 (1931).

[2] Ordinary pure aluminum which contains 99.5% of the metal has enough iron in it so that when a colloidal solution is prepared from it according to this method, iodide ion is soon oxidized to iodine, the solution becoming yellow after standing for a while. The aluminum metal which was used in this investigation was specially supplied by the Aluminum Company of America. Upon analysis it showed 99.94 ± 0.03% of aluminum.

[3] In pure water the amalgamation process is very slow.

A summary of the conditions of preparation, composition, viscosity and $P_H$ values of the sols is given in Table I. The aluminum content was determined gravimetrically as oxide and the iodine content potentiometrically.[4,5] Qualitative tests showed no iron nor mercury present.

It is noticed in Table I that the sols prepared at room temperature were quite different from those prepared in the hot. The former had lower $P_H$ values, lower viscosities and less aluminum. The amount of aluminum in a sol was determined largely by the temperature of reaction and at a given temperature a higher concentration of acid and a longer time of reaction produced sols of a higher aluminum content. Dialysis of sols increased the $P_H$ value and decreased the iodide content. While the total aluminum concentration also diminished upon dialysis, this was due more to dilution of the solution than to diffusion of aluminum compounds through the membrane.

TABLE I

PREPARATION, COMPOSITION, VISCOSITY AND $P_H$ VALUES OF THE SOLS

| | Sol I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| 0.5 *N* HI added, cc. | 20 | 25 | 50 | .. | 50 | 100 | .. | 50 |
| Total vol., liters | 3 | 3 | 3 | .. | 4 | 4 | .. | 3 |
| Temp. of reaction | Room | Room | Room | .. | Boiling | Boiling | .. | Boiling |
| Time of reaction | 2 days | 3 days | 3 days | .. | 8 hrs. | 8 hrs. | .. | 8 hrs. |
| Dialysis | .. | .. | .. | Sol I dialyzed for 10 days | .. | .. | Sol VI dialyzed for 4 days | 14 days |
| Aluminum content (millieq. per liter) | 23.0 | 59.0 | 60.2 | 8.77 | 183.9 | 425.6 | 386.9 | 143.4 |
| Iodide content | 2.961 | 3.644 | 6.099 | 0.363 | 5.320 | 11.25 | 4.511 | 1.291 |
| Ratio Al/I | 7.8 | 16.2 | 9.9 | 24.2 | 34.6 | 37.8 | 85.8 | 111.1 |
| Viscosity, time of outflow in seconds ($H_2O$ = 82.0)[a] | 82.4 | 82.5 | 82.7 | 82.6 | 87.9 | 92.3 | 109.4 | 95.6 |
| $P_H$ value | 4.20 | 4.21 | 4.31 | 5.77 | 4.88 | 4.98 | 5.05 | 5.63 |

[a] At 25° ±0.1°.

**Neutral Salt Effect on $P_H$ of the Sols.**—In studying the neutral salt effect on the hydrogen-ion activity of the sols, potassium nitrate, chloride, sulfate, acetate and oxalate were used. Since it was desired to have all

TABLE II

$P_H$ VALUES OF SALT SOLUTIONS

| Concn. normality | $KNO_3$ | KCl | $KC_2H_3O_2$ | $K_2SO_4$ | $K_2C_2O_4$ |
|---|---|---|---|---|---|
| 0.05 | 6.51 | 5.76 | .. | 6.15 | .. |
| .10 | 6.47 | 5.70 | 6.42 | 6.11 | 6.57 |
| .25 | 6.37 | 5.63 | 6.44 | 6.06 | 6.58 |
| .50 | 6.22 | 5.58 | 6.49 | 5.58 | 6.61 |
| 1.00 | .. | .. | 6.63 | .. | 6.67 |

[4] Hendrixson, THIS JOURNAL, **43**, 14 (1921).

[5] Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, New York, 1926, pp. 232–237.

the salt solutions slightly acid, 0.4 cc. of normal acetic acid was added to 1950 cc. of normal potassium acetate solution and 1.0 cc. of normal oxalic acid to 1950 cc. of normal potassium oxalate solution. The $P_H$ values of the salt solutions used are shown in Table II.

Twenty-five cc. portions of a sol were measured into 125-cc. wide-mouthed glass-stoppered bottles and to each was added an equal volume of salt solution, followed by shaking. After standing overnight, the hydrogen-ion activity of each mixture was measured by means of the quinhydrone electrode with a saturated potassium chloride–calomel cell at $25 \pm 0.1°$. A constant potentiometer reading was usually obtained within five minutes if the mixture had been previously saturated with quinhydrone and allowed to come to the temperature of the thermostat before the electrode was inserted. The readings were taken to the nearest millivolt.

When the $P_H$ value of the mixture was near or more than 8, the hydrogen electrode was used. In this case, there being invariably complete precipitation of the sol, the mixture was filtered through a dry filter paper, rejecting the first five cc. of the filtrate. (Measurements had been tried without filtering off the precipitate, but the attainment of equilibrium was exceedingly slow, due to an accumulation of gelatinous precipitate on the platinized electrode.)

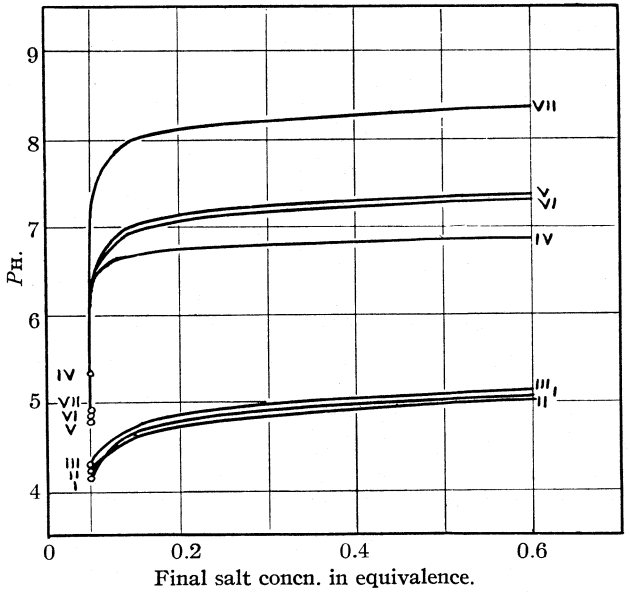



Fig. 1.—Effect of potassium sulfate on $P_H$ of sols.

Figure 1 shows that the addition of potassium sulfate produces an increase in $P_H$ value in all cases. Sols I, II and III, which had been prepared at room temperature, reacted practically alike. Sols V and VI which were prepared in the hot were more reactive, however, as were also sols IV and VII which were prepared by the room temperature dialysis of sols I and VI, respectively. The same distribution of curves was obtained upon titration

of the sols by potassium chloride, the only difference being a lower $P_H$ level throughout.

Figure 2 shows first that sols V and VI which had been prepared under like conditions reacted concordantly not only toward potassium chloride and potassium sulfate but also toward potassium acetate and oxalate; and second that different salts have widely different effects on the sols, potassium oxalate being most effective and potassium nitrate the least.

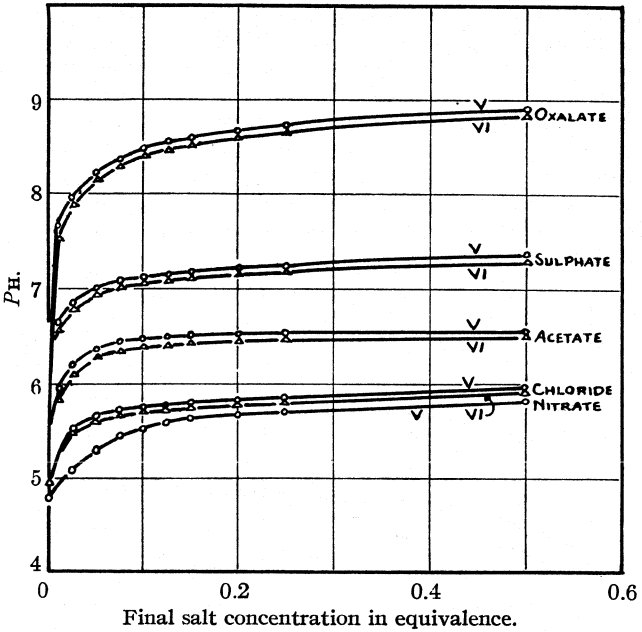



Fig. 2.—Effect of potassium salts on $P_H$ of sol V and sol VI.

It should be recalled that the solutions of potassium acetate and oxalate contained a small amount of added acid. Their effect upon dilute sols (I, II, III and IV) was tried and it was found that the whole effect was dominated by the buffer action.

Figure 3 shows the effect of different salts on the $P_H$ of sol VII. When compared with the curves for sol VI in Fig. 2, it will be noticed that for an addition of equal amounts of any salt, the effect on sol VII was greater than on sol VI. Also the order of effectiveness of anions in increasing the $P_H$ of a sol is shown to be the same.

It is noticed that there is a maximum in the acetate curve, which indicates that the buffer action of the acidified salt became dominant. From Table II it is clear that the resultant hydrogen-ion activity of the mixture was approaching that of the acetate solution as its concentration increased.

From all the results shown in Figs. 1 to 3, the following facts are evident: (1) Salts decreased the hydrogen-ion activity of the sols and in certain cases the mixtures of sols and salt solutions became quite alkaline. (2) The order of effectiveness of the anions in increasing the $P_H$ of the sols was found to be: nitrate < chloride < acetate < sulfate < oxalate. (3) On addition of different salts, sols I, II and III were quite alike in reaction, as were also sols V and VI, despite the fact that they had been prepared by the reaction of different amounts of acid for different lengths of time, and that they differed considerably in their aluminum and iodide contents. Those which reacted similarly were those which had been prepared at the same temperature. (4) Sols which were prepared at high temperature and dialyzed sols were more reactive toward the salts.

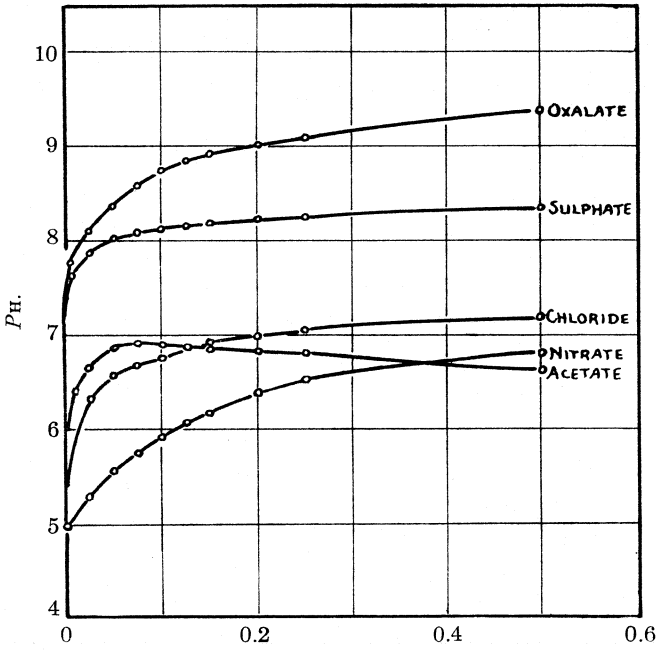



Fig. 3.—Effect of potassium salts on $P_H$ of sol VII.

**Salt Effect upon Sols of Different Basic Aluminum Salt Complexes.**—Four different sols—aluminum oxyiodide, bromide, chloride and acetate—were prepared for comparison. The procedure of preparation was as follows: 25 cc. of 0.5 *N* acid was added to 3 liters of distilled water containing four pieces of clean amalgamated aluminum of about 150 g. each and heated to 90° (thirty-five minutes required) and this temperature was maintained with a maximum variation of 3° for one hour, when the resulting solution was cooled in running water. Then it was allowed to

stand at room temperature for one day, and centrifuged for an hour. Analytical data are given in Table III.

TABLE III

COMPOSITION OF BASIC ALUMINUM SALT SOLS

Values given are milliequiv. per liter

| Sols | Oxyiodide | Oxybromide | Oxychloride | Oxyacetate |
|---|---|---|---|---|
| Aluminum | 60.9 | 70.9 | 80.2 | 18.01 |
| Anion | 3.27 | 3.50 | 3.54 | 2.53 |

The effects of potassium chloride and sulfate upon these sols are plotted in Figs. 4 and 5.

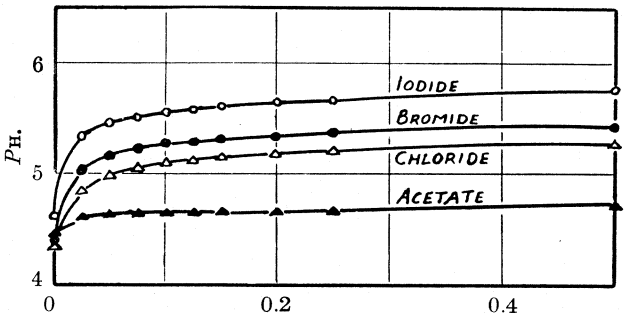



Fig. 4.—Effect of potassium chloride on $P_H$ of different aluminum oxy sols.

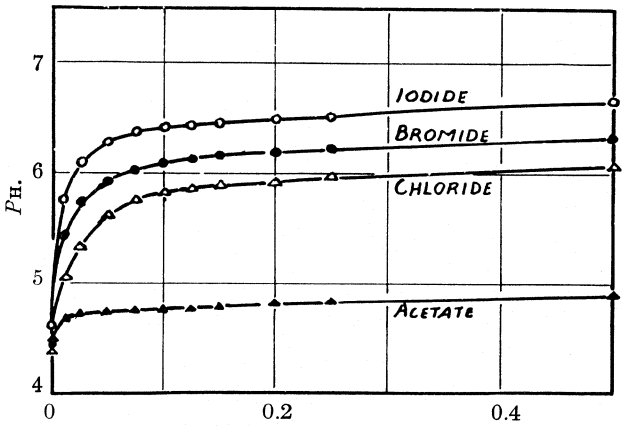



Fig. 5.—Effect of potassium sulfate on $P_H$ of different aluminum oxy sols.

Both Fig. 4 and Fig. 5 show that on addition of equal amounts of the same salt, the effect on the $P_H$ of the sols is markedly different, the order

from most reactive to least being aluminum oxyiodide sol > oxybromide > oxychloride > oxyacetate. It is quite interesting to compare this order with that of the effectiveness of potassium salts of these anions in increasing the $P_H$ values of aluminum oxychloride sols as found by Thomas and Whitehead,[1] namely, acetate > chloride > bromide > iodide. Hence, the anion which is more effective in increasing the $P_H$ of aluminum oxychloride sols makes a sol less sensitive toward the action of salts when it is part of the composition of the sol.

**Effect of Aging and Heating of the Sols.**—Portions of sols I, IV and V, in "Non-Sol" bottles, were stored at 90° for ten days. Then they were cooled to 25° and the $P_H$ values were determined immediately and at various intervals thereafter together with the $P_H$ values of portions of the same sols which had not been heated, as shown in Table IV.

TABLE IV

CHANGE OF $P_H$ OF THE SOLS ON AGING AND HEATING

| Age in days | Sol I | | Sol IV | | Sol V | |
|---|---|---|---|---|---|---|
| | Not heated | Heated | Not heated | Heated | Not heated | Heated |
| 0 | 4.20 | 3.15 | 5.77 | 4.14 | 4.88 | 4.07 |
| 1 | .. | 3.17 | .. | 4.20 | 4.88 | 4.13 |
| 5 | 4.16 | .. | 5.75 | .. | .. | .. |
| 10 | .. | 3.28 | 5.67 | 4.42 | 4.80 | 4.26 |
| 14 | 4.10 | .. | .. | .. | .. | .. |
| 20 | .. | 3.31 | .. | 4.48 | .. | 4.28 |
| 50 | 3.94 | .. | 5.59 | .. | .. | .. |
| 90 | 3.87 | .. | .. | .. | 4.58 | .. |

The figures in the first line of Table IV show a considerable decrease in the $P_H$ values of the sols as a result of the heating. Aging of the original sol at room temperature had the same effect although to a much less extent. Sol I became milky in appearance at the end of heating for ten days, while a partial precipitation occurred in sol V. No change in appearance was observed in sol IV.

The change in $P_H$ of the heated sols on subsequent aging at room temperature is significant. All the original unheated sols, no matter whether prepared at room temperature or at a higher temperature, decreased in $P_H$ while the same sols after heating increased gradually in $P_H$ while standing at room temperature.

The neutral salt effect on that portion of sol I which had been heated at 90° for ten days is given in Fig. 6.

It is evident from Fig. 6 that heating not only increased the hydrogen-ion activity of the sol but made it much less sensitive toward the action of salts.

**Conductance Titrations of the Sols.**—If it is accepted that the order of

the effects of the anions previously described in this investigation represents their tendency to penetrate into the complex ol-compound of which the colloidal micelle is constituted, then conductivity measurements upon aluminum oxyiodide sols under titration with silver salts should show the same order.

Silver nitrate, sulfate, acetate and tartrate were used. Weighed portions of these salts were placed in 250-cc. "Non-Sol" bottles; 100-cc. portions of sol were then pipetted into these bottles. Silver nitrate and silver acetate dissolved readily while silver sulfate and tartrate required two to three days for solution even with occasional vigorous shaking. During all operations with the silver salts the usual precautions concerning exposure to actinic rays were observed.

After complete solution of the silver salt, the conductivity was measured at 25 $\pm 0.01°$ in a cell provided with bright platinum electrodes.

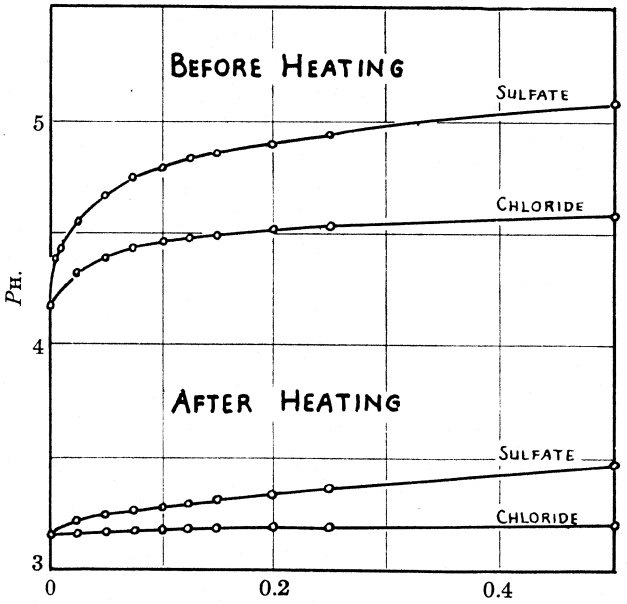



Fig. 6.—Salt effect on $P_H$ of sol I (before and after heating).

The results obtained with sols V and VIII are plotted in Figs. 7 and 8.

In these figures the point of intersection of the two branches of each curve corresponds to the completion of the reaction: $Ag^+ + I^- = AgI$. It is significant that not only do the points agree with each other but they agree also with the value of the iodide content of the sol as determined by the potentiometric method.

It is significant too that before the intersection point is reached, each curve approaches it with a different slope and that at the point where the equivalent amount of salt had been added, the conductivities of the mix-

tures were widely different, nitrate having the highest value and tartrate the lowest.

Although the sulfate and tartrate curves in Figs. 7 and 8 are quite close to each other, the difference in the decrease of conductivities after the addition of these silver salts was definite. The last point for silver tartrate does not fall on the curve, as is seen in both figures. This was due to some change taking place as revealed by the color of the mixture becoming quite brown after the dissolution of the salt was completed, which will be discussed later.

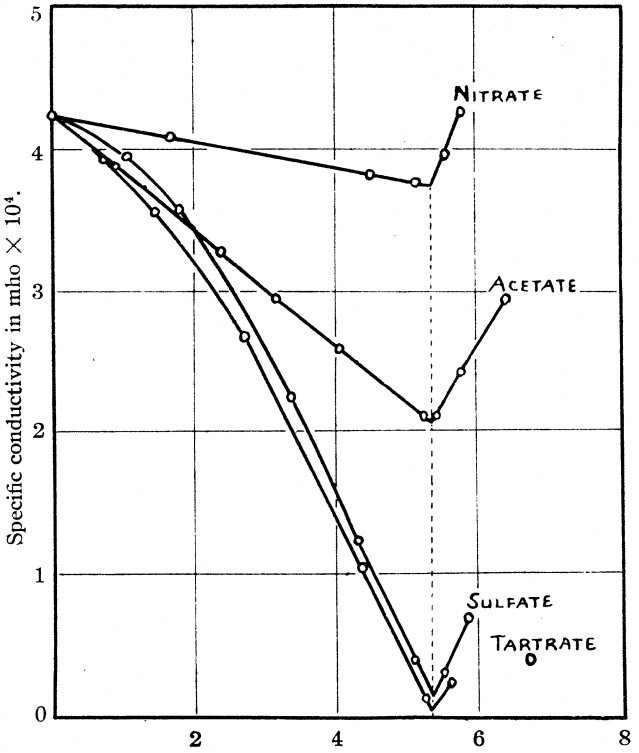



Fig. 7.—Conductance titrations of sol V.

It should be noticed that sol VIII was prepared in the hot and then dialyzed at room temperature for two weeks. Its conductivity was about one-seventh that of sol V. The iodide content of the two sols differed widely too and this difference is considered responsible for the slight difference in the shape of the two sulfate curves.

From both figures, the following facts are evident. All the iodide in the sol was replaceable by nitrate, acetate, sulfate and tartrate ions equally

since the values of the iodine content of a sol determined by the conductance method agreed with each other as well as with the analytical result; when an amount of silver salt equivalent to the iodide content of the sol was added, the conductivity reached a minimum; and the magnitude of the decrease in conductivity was dependent upon the anion of the silver salt, the order being: nitrate < acetate < sulfate < tartrate.

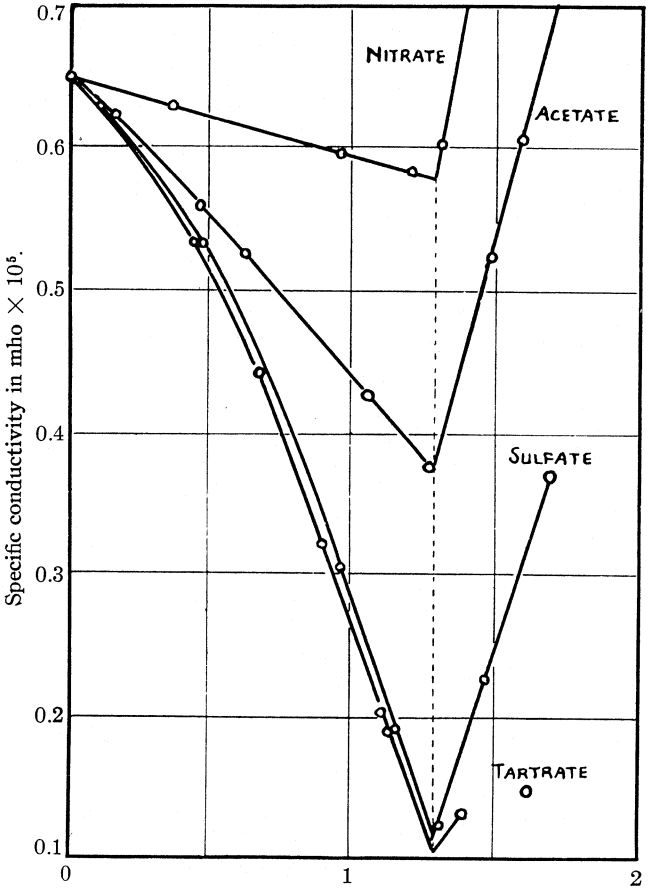



Fig. 8.—Conductance titrations of sol VIII.

Other things being equal, the conductivity of a solution depends upon the mobilities of the ions present. The mobilities of the anions are in the order: sulfate > iodide > nitrate > acetate > tartrate. In Figs. 7 and 8, the differences in the slopes of the curves before the intersection point show the difference in rates of conductivity decrease of the sols on addition of different silver salts. When silver nitrate or silver acetate is added, the

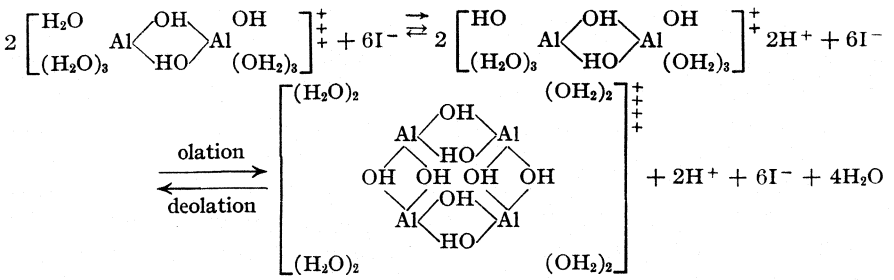
decrease in conductivity may be accounted for by the fact that fast moving iodide ions outside the nucleus have been replaced by the comparatively slowly moving nitrate or acetate ions. However, with silver tartrate, the conductivity at the equivalent point was about 16% of the original value in the case of sol VIII and only 1% in the case of sol V. The difference in the mobilities of the iodide and tartrate ions alone cannot account for this drop in conductivity. A more significant point is that despite the fact that sulfate ion has a higher mobility than iodide, before the equivalent point had been reached, the conductivity of the sol was very rapidly diminished by silver sulfate. Therefore, it must be assumed that in some way most of the fast moving sulfate ions must have disappeared. This is also true for the tartrate ions and to some extent for the acetate ions. For reasons which will be explained later, it is believed that if any nitrate ion so disappeared, the amount must have been very small.

**Interpretation of Results and Summary.**—Based on Werner's theory as extended by Bjerrum[6] and Stiasny[7] to account for the behavior of solutions of basic chromium salts, the statements made in an earlier paper[1] give a consistent and satisfactory explanation for the results obtained in this investigation.

An examination of the composition of the sols (Table I) will reveal the fact that the aluminum content of each sol greatly exceeded the iodide content, especially in those sols which had been prepared in the hot. In sol VII, for example, to every mole of iodide, there were roughly 28 moles of aluminum. Accordingly these sols may be considered to consist of highly basic aluminum salt mixtures. On standing, the process of olation took place and resulted in a gradual increase of hydrogen-ion activity (Table IV). As the sol was heated, olation took place more rapidly. Oxolation to some extent was effected, too. All of these changes tended to increase the hydrogen-ion activity of the solution. The acidity of a heated sol became much higher in ten days than that of the same one, not heated, in ninety days. However, after the heated sol had been cooled, aging produced the opposite effect, that is, hydrogen-ion activity decreased, because at a lower temperature, the degree of dissociation of aquo groups in the complex decreased, on one hand, and, on the other, an excess of acid reacted with some of the ol-linkages which had been formed on heating and converted them to hydroxo groups which are supposed to be more reactive than the ol-groups. This process, which is a reverse of olation, is termed "deolation." By way of illustration, possible reactions undergone by a hypothetical compound of hepta-aquo-mono-hydroxo-diol-dialumini triiodide, on heating, are pictured as follows

[6] Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907).

[7] Stiasny and co-workers, *Collegium*, **657**, 190 (1925); **670**, 41 (1926); **682**, 86 (1927); **694**, 49 (1928); **694**, 72 (1928); **694**, 97 (1928).




The last product may further dissociate and be olated to form still more complicated complexes as well as undergo the process of oxolation. Processes of olation and oxolation will result in the formation of less hydrated and more complex particles, *e. g.*, after heating for ten days, turbidity resulted in sol I and partial precipitation in sol V.

Sols of basic aluminum salts are regarded as formed from positively charged complex aluminum hydrates which dissociate into basic aluminum ionic micelles and hydrogen ions. It might be contended that the addition of a neutral salt would result in the so-called "negative secondary salt effect," that is, the degree of dissociation of the complex alumina hydrates would be decreased by the added salt and, consequently, the hydrogen-ion activity of the solution would decrease. However, the increase of the $P_H$ values of the sols on addition of neutral salts cannot be explained by this idea of change of equilibrium between basic aluminum ionic micelles and hydrogen ions, because the reaction between neutral salts and basic aluminum compounds has been demonstrated to be of a different nature. Feigl and Krauss[8] have shown that a solution of aluminum chloride is rendered neutral by the addition of potassium oxalate

$$AlCl_3 + 3K_2C_2O_4 = K_3[Al(C_2O_4)_3] + 3KCl$$

while a solution of basic aluminum acetate is rendered alkaline

$$Al(OH)(C_2H_3O_2)_2 + 3K_2C_2O_4 = K_3[Al(C_2O_4)_3] + 2KC_2H_3O_2 + KOH$$

and utilize these reactions in the analysis of aluminum solutions.

Passing now from such simple crystalloid solutions to gels, it may be pointed out that when freshly precipitated alumina hydrate is treated with a neutral salt such as potassium or sodium sulfate, citrate, phosphate, etc., the solution becomes alkaline to phenolphthalein.[9] Furthermore, Weiser[10] has found that in the precipitation of aluminum oxyacetate hydrosol by salts, the anions of the added salts are removed in definite amounts from the solution by the gel.

The facts just mentioned indicate that the anions combined with the basic aluminum complex and displaced hydroxyl ions therefrom. The

[8] Feigl and Krauss, *Ber.*, **58B**, 398 (1925).

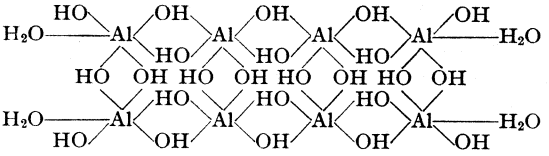
[9] Sen, *J. Phys. Chem.*, **31**, 691 (1927).

[10] Weiser and Middleton, *ibid.*, **24**, 630 (1920).

amount of the latter displaced depends first of all on the penetration power of the anions added. Based on the effectiveness in increasing the $P_H$ values of the sols, the penetration order of the anions that were studied in this investigation is: nitrate < chloride < acetate < sulfate < oxalate.

By the amalgamated aluminum method, it was found that sols which had been prepared at the same temperature and under similar conditions reacted quite alike toward neutral salts. The probable mechanism of the formation of sols with this method can be divided into two steps: the production of alumina hydrate by the action of water upon amalgamated aluminum and the peptization of the hydrate by the acid that is present.

Neogi and Mitra[11] analyzed alumina hydrate that had been prepared from the aluminum–mercury combination and found it had a definite composition. They expressed the results of their analysis by the formula $Al_2O_3 \cdot 4H_2O$. According to the idea which is adopted in this paper, the simplest two dimensional structure of the compound corresponding to the above formula is



At the outset, in the presence of an acid, two possible reactions are expected to take place with this compound. Hydrogen ions react with the hydroxo groups (shown at the four corners in the picture above) to form aquo groups and deolation may take place to some extent. A certain number of the anions that are present in the solution may also enter the complex and displace an equivalent number of water molecules, or hydroxo groups, or both. As the reaction proceeds, the amount of free acid decreases. Finally, when an excess of freshly formed alumina hydrate is present, the solution will reach a state of approximately constant concentration of hydroxo groups in the complex aluminum ions. At a higher temperature of preparation, the solution will contain more of the hydroxo groups; because at a higher temperature the aluminum complex dissociates to a greater extent than at a lower temperature. The hydrogen ion formed as a result of this more extensive dissociation will react with the freshly produced aluminum hydroxide and, consequently, cause more aluminum to be dispersed.

The increase in the $P_H$ values of the sols upon addition of neutral salts is due primarily to the replacement of hydroxo groups by the anions of the added salts. Since sols which had been prepared at higher temperatures

[11] Neogi and Mitra, *J. Chem. Soc.*, 1222 (1927).

contained more hydroxo groups than those which had been prepared at lower temperatures, neutral salts had greater effect upon the former sols (Fig. 2 and Table I).

Dialysis removes hydrogen ion and its equivalence of anion from the sol. This is indicated by the increase in $P_H$ of the solution upon dialysis. Thus, the equilibrium between hydroxo groups inside of the complex and hydrogen ions outside, and that of the anions on both sides, was disturbed. Further dissociation was favored, which resulted in the formation of more hydroxo groups and removal of the anion from the inside of the complex. The sensitivity of the sol toward the action of neutral salt was thus increased (Figs. 1, 2 and 3, and Table I).

An ol-group in a complex aluminum ion is much less readily displaced by anions than an hydroxo group, and an oxo group is not displaced at all. Heat increases olation and oxolation. A heated sol, therefore, becomes much less reactive toward neutral salts than the original one (Fig. 6).

The penetration order of the halides and acetate was found to be: iodide < bromide < chloride < acetate. Since at equal concentrations, a highly penetrating ion will enter the complex to a greater extent than a less highly penetrating ion, then more hydroxo groups should be expelled from the nucleus in the former than in the latter case. When prepared under similar conditions, the micelles of aluminum oxyacetate sol should contain fewer hydroxo groups than an oxyiodide sol. On addition of equal amounts of neutral salts, oxyiodide sol consequently gave a larger increase in $P_H$ than oxyacetate sol, while oxychloride and oxybromide sols gave intermediate values of increase (Figs. 4 and 5).

Now, the explanation of the results of the conductivity experiments becomes evident. The cause of the decrease of conductivity upon addition of silver salts cannot be attributed alone to the fact that highly mobile iodide ions in solution were substituted by the less mobile ones, because, as has already been pointed out, sulfate ion has higher mobility than iodide, yet the decrease in conductivity on addition of silver sulfate was one of the most marked (Figs. 7 and 8). Sulfate ion is a very powerful penetrant. Before the amount equivalent to that of iodide in the sol was added, nearly all of it penetrated into the complex and, therefore, no longer affected the conductivity. The entering sulfate ions replaced aquo, iodo and hydroxo groups from the complex. The replacement of aquo groups caused a decrease in the charge of the micelles, thus resulting in a decrease in their effect upon the conductivity. The iodide ion formed by the displacement of iodo groups was precipitated as silver iodide and the hydroxyl ion from the displaced hydroxo group combined with the hydrogen ion in solution. Nitrate and acetate ions are less penetrating than sulfate ions, and consequently the slopes of their curves are not so steep.

Since the amounts of silver salts added to the sols in these conductivity

experiments were very small, no free hydroxyl ion (in excess of hydrogen ion) should be present in the solution. For example, the maximum amount of silver salt added to sol V was less than 0.007 equivalent per liter. According to Fig. 2, at such a concentration of the added anions—nitrate, acetate and sulfate—the solutions were still acid. However, oxalate ion at that concentration would displace hydroxo groups from the complex to such an extent as to bring the solution to a $P_H$ value of about 7.5. Since tartrate ion, similar to oxalate ion, is a more powerful penetrant than sulfate ion, a small amount of it would be sufficient to displace enough hydroxo groups to make the solution alkaline. In the conductivity experiments, the brown coloration observed in each of the final mixtures of silver tartrate and sols V and VIII is presumed to be due to the formation of silver hydroxide.

From the results of conductivity experiments, the penetration order of the anions studied should be: nitrate < acetate < sulfate < tartrate. The fact that nitrate ion, less penetrative than iodide, replaced all the iodide in the sol does not exclude the possibility of having a fraction of the total iodide inside of the complex in the original sol, since the mixture of the sol and silver nitrate was allowed to stand for two days. As soon as the iodide ions on the outside are removed by precipitation, some of the iodide inside of the complex migrates out to restore the equilibrium and so on until all is removed from the complex.

Results of the measurements of salt effect on $P_H$ and conductivity of sols have shown the anion penetration order to be: nitrate < chloride < acetate < sulfate < oxalate, tartrate. This order is identical to that found by Thomas and Whitehead for aluminum oxychloride sols and to the anion penetration order of Stiasny for solutions of basic chromium salts, except that the positions of sulfate and acetate are interchanged.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE POND CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

# THE STICK ANTIMONY ELECTRODE: PREPARATION AND CALIBRATION[1]

BY L. R. PARKS AND H. C. BEARD

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## Introduction

The stick antimony electrode has been recognized as being a practical and useful method for electrometric titrations and the measurement of hydrogen-ion concentration of solutions which cannot be determined by either the hydrogen or the quinhydrone electrodes, notably colloids and dyestuffs. It is much sturdier than the glass electrode and calibration before each measurement is not essential.

When a metal is in equilibrium with its oxide, which is slightly soluble in solution, an electrode potential is set up which is a measurement of the hydrogen-ion concentration of that solution.[2] The electrode used in this investigation was a cleaned and polished metallic stick. The antimony trioxide is present as an adsorbed film on the metal. This film is formed easily and rapidly in dry air.[3] The presence of moisture aids in the formation of this film.[4] Kolthoff and Hartong, Roberts and Fenwick[5] and Britton and Robinson[6] added antimony trioxide to the solution to be measured. Franke and Willaman[7] and Snyder[8] were among the first to use the stick antimony metal as an electrode without the use of the added oxide.

Uhl and Kestranek[9] kept the solution in motion by passing in washed air. This procedure of keeping the liquid in motion has been carried on by other investigators using different methods. Kolthoff and Hartong state that an inert gas, as nitrogen or hydrogen, may be used. However, mechanical stirring has been employed by the majority of investigators. Franke and Willaman prefer "stirring without unnecessary agitation" while Britton and Robinson state that vigorous stirring gives best results.

[1] This paper is a portion of a thesis offered by H. C. Beard in partial fulfilment of the requirements for the M. S. degree in the School of Chemistry and Physics at the Pennsylvania State College.

[2] Kolthoff and Hartong, *Rec. trav. chim.*, **44**, 113 (1925).

[3] Tammann, *ibid.*, [4] **4**, 546 (1923).

[4] Ditte and Metzner, *Compt. rend.*, **115**, 938 (1892); Thiele, *Ann.*, **263**, 361 (1891); Ruff and Albert, *Ber.*, **38**, 54 (1908); Milbauer and Slemr, *Chem. Listy*, **20**, 392 (1926); Clarke, *Analyst*, **54**, 99 (1929); Grant, *ibid.*, **54**, 227 (1929).

[5] Roberts and Fenwick, THIS JOURNAL, **50**, 2125 (1928).

[6] Britton and Robinson, *J. Chem. Soc.*, 458 (1931).

[7] Franke and Willaman, *Ind. Eng. Chem.*, **20**, 87 (1928).

[8] Snyder, *Soil Science*, **26**, 107 (1928).

[9] Uhl and Kestranek, *Monatsh.*, **44**, 29 (1923).

Brewer and Montillon[10] bubbled nitrogen through a closed electrode vessel while Snyder used a closed mechanical shaking electrode system. Unstirred solutions were used in this investigation.

Cast electrodes were prepared as suggested by Franke and Willaman. Attempts were made to increase the oxide film but the electrodes gave best results when polished clean with emery cloth and rinsed with distilled water. Using the simple potentiometric method with these electrodes it was impossible to get a stable point of equilibrium due to drifting of the potential. This drifting seemed to be almost a definite variable, which was probably due to polarization of the electrode. Drifting was greatest in the acid and alkaline ranges and least in the neutral range.

In order to overcome any possible effects due to polarization, a vacuum-tube potentiometer, such as is used with glass electrodes, was constructed. Since the function of a vacuum-tube potentiometer is to cut down to a minimum the flow of current to the electrode, polarization is also reduced to a minimum. By using this system, antimony electrodes in an unstirred buffer solution gave a stable reproducible equilibrium point very quickly.

It is the purpose of this investigation to show that, with the use of the vacuum-tube potentiometer, stick antimony electrodes in unstirred solution in contact with air may be calibrated against buffer solutions of different $P_H$ values to give a curve which agrees with that of the hydrogen electrode as to slope, thus satisfying the Nernst equation, from the $P_H$ value of 2 to that of 7. Advantages of this system, due to the prevention of polarization, are noted and the effect of the stirring or the bubbling of a gas through the solution is discussed.

## Experimental Apparatus and Procedure

The electrodes were cast from Mallinckrodt's C. P. and Baker's C. P. analyzed antimony in glass tubes of 6 mm. bore. In some cases the electrodes were cooled very slowly in a temperature controlled furnace and in other cases they were allowed to cool normally to the temperature of the room. With the slow cooling sticks large crystals of the metal were obtained and with the rapid cooling fine crystals, as was noted by Bekier.[11] Electrical connections were made to the antimony electrode by soldering on a piece of copper wire to one end of the stick. The electrodes varied in length from 6 to 13 cm. In use they were immersed in the buffer solution to a depth of about 4 cm. They were always polished bright and clean with fine emery cloth and rinsed with distilled water just before using. Eight different electrodes were used and compared in the course of the investigation.

The buffer solutions used were Clark and Lubs' standard mixtures, Sørensen's standard glycocoll mixtures, and Ringer's mixtures.[12] All of these buffer solutions were checked with a hydrogen electrode.

The apparatus used in the determinations was the standard Hydrogen-Ion Po-

[10] Brewer and Montillon, *Trans. Am. Electrochem. Soc.*, **55**, 356 (1929).

[11] Bekier, *Z. anorg. Chem.*, **78**, 178 (1912).

[12] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 1928, 3d ed.

tentiometer Outfit of Leeds and Northrup using the saturated calomel cell. The standard cell was checked against one calibrated by the Bureau of Standards. Several calomel cells were carefully made and frequently checked against each other. The mercury was purified by the method of Hulett.[13] The vacuum-tube potentiometer is of a design developed by E. A. Lantz of the Hercules Powder Company.

All measurements were taken at a temperature of 25°.

## Experimental Data

**A. With the Use of the Potentiometer.**—Readings were taken with the potentiometer and the vacuum-tube potentiometer separately for the purpose of comparison. With the potentiometer alone, in acid, neutral and alkaline buffer solutions, there was considerable instability of the point of equilibrium. In some cases a peak was obtained and in others not. Readings were taken at minute intervals.

The drifting is not very great but it is a question of just what is the correct value. Comparative readings with buffer solutions of different $P_H$ values may be taken at the end of a specified time but it is no criterion as to the accuracy of the results.

These same solutions were also measured using the vacuum-tube potentiometer for comparison as noted in Table I.

TABLE I

COMPARISON OF RESULTS WITH THE POTENTIOMETER AND THE VACUUM-TUBE POTENTIOMETER

| $P_H$ | Vacuum-tube potentiometer v. | Potentiometer (5 min. rdgs.), v. | Difference, mv. |
|---|---|---|---|
| 2.32 | 0.1297 | 0.1287 | 1.0 |
| 4.97 | .2861 | .2848 | 1.3 |
| 7.67 | .4469 | .4462 | 0.7 |
| 10.70 | .6048 | .5972 | 7.6 |

It is noticeable that the difference is slight in the $P_H$ range of 2 to 8 but of considerably greater value in the alkaline range. These results would seem to justify the use of the potentiometer only in the former range to get acceptable values for general purposes.

**B. Readings with the Vacuum-tube Potentiometer.**—Readings made with the vacuum-tube potentiometer were very constant. The equilibrium point was obtained only in the time it took to balance the apparatus, which was rarely over a minute. The accuracy of the instrument is about 2 mv. and this would be the only deviation from the equilibrium point in prolonged readings. Readings were taken to tenths of a millivolt so that a more accurate average of all of the different electrodes would be obtained. There was no evidence of any drifting, except possibly in the high alkaline range where the electrode no longer gives a true measurement of the hydrogen-ion concentration.

[13] Hulett, *Phys. Rev.*, **21**, 388 (1905).

There was no attempt made to use either the electrodes or the buffer solutions in any particular order, as advised by Roberts and Fenwick. The readings were taken over a period of several weeks and are brought together in Table II. The readings in all cases are definite equilibrium points obtained and not averages.

It is notable that all of these electrodes, made at different times under different conditions, should give such concordant results. The greatest deviation of any electrode from the average is 3.5 mv. except in the high alkaline range. It will be noticed that in the high alkaline and acid ranges there seems to be a grouping of the electrodes, A, B and D giving high readings while the other group gives lower. Upon examination of the electrodes it was found that those of the former group were of large crystalline structure while those of the latter were made up of fine crystals. This is in agreement with Getman,[14] who found that cadmium electrodes of a large crystal give higher potential readings than those of a fine polycrystal structure.

TABLE II

THE MEASURED E. M. F. OF THE CELL Sb | $Sb_2O_3$, SOLUTION || SATD. KCl, $Hg_2Cl_2$ | Hg WITH DIFFERENT STICK ANTIMONY ELECTRODES

| | Electrodes | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $P_H$ | A v. | B v. | C v. | D v. | K v. | M v. | N v. | O v. | Av. v. | Max. dev. from av., mv. |
| 1.30 | 0.0768 | 0.0800 | 0.0822 | 0.0817 | 0.0777 | 0.0760 | 0.0768 | 0.0777 | 0.0786 | 3.6 |
| 1.60 | .0912 | .0896 | .0898 | .0896 | .0896 | .0889 | .0938 | .0938 | .0908 | 3.0 |
| 2.24 | .1250 | .1290 | .1290 | .1250 | .1250 | .1250 | .1250 | .1290 | .1265 | 1.5 |
| 2.98 | .1689 | .1711 | .1712 | .1700 | .1680 | .1681 | .1690 | .1691 | .1694 | 1.8 |
| 3.98 | .2275 | .2297 | .2284 | .2279 | .2259 | .2295 | .2266 | .2283 | .2280 | 2.1 |
| 4.97 | .2868 | .2884 | .2876 | .2839 | .2839 | .2868 | .2870 | .2847 | .2861 | 2.3 |
| 7.00 | .4076 | .4077 | .4082 | .4032 | .4077 | .4030 | .4046 | .4060 | .4060 | 3.0 |
| 7.87 | .4592 | .4532 | .4568 | .4581 | .4535 | .4570 | .4522 | .4552 | .4557 | 3.5 |
| 8.81 | .5003 | .5003 | .4976 | .4997 | .5008 | .5010 | .5008 | .4985 | .4999 | 2.3 |
| 9.81 | .5541 | .5510 | .5519 | .5509 | .5508 | .5518 | .5510 | .5510 | .5516 | 2.5 |
| 10.53 | .5939 | .5947 | .5938 | .5948 | .5938 | .5947 | .5939 | .5930 | .5941 | 1.1 |
| 11.29 | .6588 | .6548 | .6506 | .6580 | .6553 | .6506 | .6482 | .6530 | .6537 | 5.5 |
| 11.86 | .7283 | .7344 | .7213 | .7283 | .7223 | .7215 | .7189 | .7210 | .7240 | 10.4 |
| 12.01 | .7678 | .7774 | .7608 | .7736 | .7570 | .7608 | .7509 | .7618 | .7638 | 13.6 |

Since an equilibrium point was reached so nicely with an unstirred solution, experiments were performed to find the effect of stirring the solution and also the bubbling of so-called inert gases.

These experiments showed that stirring lowers the potential and the amount of change is proportional to the rate of stirring. Stirring affects the solution in at least two ways. It increases the concentration of potassium chloride in the solution by causing currents to flow past the saturated potassium chloride junction of the calomel electrode. Stirring also naturally increases the amount of air, and thus of oxygen, in the solu-

[14] Getman, *J. Phys. Chem.*, **35**, 588 (1931).

tion. Harrison and Vridhachalam[15] and Snyder also note that the potentials obtained in unstirred solutions are somewhat higher than those in stirred solutions. Procopiu[16] states that the movement of an electrolyte with reference to a metal electrode causes an electromotive force.

It was found, by experimentation, that bubbling a gas through the buffer solution, when in contact with the stick antimony electrode, made a considerable difference in the potential obtained. Nitrogen, hydrogen, oxygen and air were bubbled through fresh buffer solutions. With all of these gases equilibrium points were obtained by the use of the vacuum-tube potentiometer within a few minutes. There is little doubt that in these cases a gas–metal electrode has been formed. French and Kahlenberg[17] state that with a gas–metal electrode the "total combination potential is due both to absorbed gas and to a condensed film of gas on the surface of the metal." The potential "depends on the gas dissolved in the electrolyte and not that in the gas phase." They also state that oxygen tends to make the metal potentials less basic, while nitrogen and hydrogen have the opposite effect. This was found to be the case with these gases in use with the antimony electrode. Bubbling of a gas and stirring tend to prevent the formation of a film of gas about the electrode and so a lower potential results than when the solution is at rest, saturated with the dissolved gas.

## Discussion

The value of the potential developed in an oxidation–reduction reaction is calculated by the Nernst equation

$$E = E_0 - \frac{RT}{NF} \ln C$$

The value of $E_0$ is a constant depending on the electrode system. The potential of any electrode system which functions to measure hydrogen-ion concentration may be determined by the Nernst equation

$$E = E_0 - \frac{RT}{F} \ln (H^+)$$

This being the case, any change in $E$ represents a change in the hydrogen-ion concentration. As the equation

$$E = E_0 - \frac{RT}{F} \ln (H^+) = E_0 - 2.3 \frac{RT}{F} \log (H^+)$$

and since the term $2.3\,RT/F$ at 25° has the value of 0.05915, noted by Lewis and Randall[18] and $P_H = -\log (H^+)$, the equation $E = E_0 + 0.05915\,P_H$ is obtained.

[15] Harrison and Vridhachalam, *Mem. Dept. Agr. India, Chem. Ser.*, **10**, 157 (1929).

[16] Procopiu, *Z. physik. Chem.*, **A154**, 322 (1931).

[17] French and Kahlenberg, *Trans. Am. Electrochem. Soc.*, **54**, 163 (1928).

[18] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.

When $E$ is plotted against $P_H$ and $E_0$ is a constant, the slope of the line should be 0.05915. As shown in Fig. 1 this holds true for the stick antimony electrode in unstirred solutions in contact with air between the $P_H$ values 2.2 to 7.8. The line for this electrode passing through these points intercepts the abscissa at the value of $-0.007$ v. Below the $P_H$ value of 2.2 and above the $P_H$ of 7.8 the stick antimony electrode does not function to measure correctly hydrogen-ion concentration.

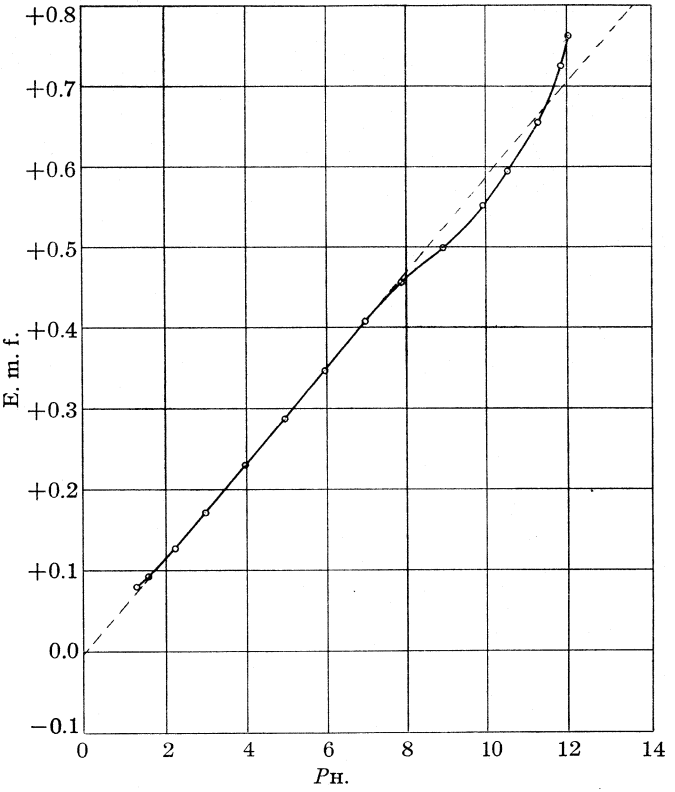


Fig. 1.—Calibration curve for the stick antimony electrode.

In Table III the value of $E_0$ is calculated from the observed value of $E$. Since $E_0 = E + 0.05915\ P_H$, the value of $E_0$ may be calculated from the equation $E_0 = E - 0.05915\ P_H$, using the $P_H$ values obtained with the hydrogen electrode. Since $E$ is the value obtained with the saturated calomel electrode, $E_0$ is the potential of the stick antimony electrode referred to the saturated calomel electrode.

The average value of $E_0$ from $P_H$ 1.60 to 7.87 of the cell Sb | $Sb_2O_3$, Solution || satd. KCl, $Hg_2Cl_2$ | Hg is $-0.0070$ v. The average of the $E_0$ values from $P_H$ 2.24 to 7.00 is $-0.0071$ v. The value taken for the calculation of

TABLE III

$E_0$ AND $P_H$ VALUES WITH THE STICK ANTIMONY ELECTRODE

| $P_H$ (Table I) | $E$ (obs.), v. | $E''$ (0.05915 $P_H$), v. | $E_0$ ($E - E''$), v. | $P_H$ ($Sb/Sb_2O_3$), calcd. | $P_H$ Diff. (Sb to $H_2$) |
|---|---|---|---|---|---|
| 1.30 | 0.0786 | 0.0769 | +0.0017 | 1.45 | +0.15 |
| 1.60 | .0908 | .0946 | − .0038 | 1.65 | + .05 |
| 2.24 | .1265 | .1325 | − .0060 | 2.26 | + .02 |
| 2.98 | .1694 | .1763 | − .0069 | 2.98 | .00 |
| 3.98 | .2280 | .2354 | − .0074 | 3.97 | − .01 |
| 4.97 | .2861 | .2940 | − .0079 | 4.96 | − .01 |
| 5.96 | .3459 | .3525 | − .0066 | 5.97 | − .01 |
| 7.00 | .4060 | .4141 | − .0081 | 6.98 | − .02 |
| 7.87 | .4557 | .4655 | − .0098 | 7.82 | − .05 |
| 8.81 | .4999 | .5211 | − .0212 | 8.57 | − .24 |
| 9.81 | .5516 | .5803 | − .0287 | 9.44 | − .37 |
| 10.53 | .5941 | .6228 | − .0287 | 10.16 | − .37 |
| 11.29 | .6537 | .6678 | − .0141 | 11.17 | − .12 |
| 11.86 | .7240 | .7015 | + .0225 | 12.36 | + .50 |
| 12.01 | .7638 | .7104 | + .0534 | 13.03 | +1.02 |

the $P_H$ of the antimony electrode is −0.007 v. Thus the Nernst equation for this electrode at 25° in this range of $P_H$ values is $E = -0.007 + 0.05915\ P_H$ when the antimony electrode is measured against a saturated calomel electrode, considering $E$ to be positive when the saturated calomel electrode is positive.

Since the normal calomel electrode referred to the hydrogen electrode is 0.037 v. more positive than the saturated calomel electrode to the same reference,[19] the Nernst equation referring to the normal calomel electrode becomes $E' = + 0.030 + 0.05915\ P_H$, considering $E'$ positive when the normal calomel is positive.

The value of $E_0$ as calculated with the saturated calomel electrode agrees well with the intercept of the curve with abscissa as shown in Fig. 1. It will be noticed that the greatest deviation of the antimony electrode from the hydrogen electrode between the $P_H$ values of 2.2 and 7.0, inclusive, is $\pm 0.02\ P_H$, and between the $P_H$ values of 1.6 and 7.8 is $\pm 0.05\ P_H$.

Upon examination of the curve of Fig. 1 it will be noticed that the nature of the curve varies with different degrees of $P_H$. It is only where the curve is straight and of the proper slope (from $P_H$ 2 to 7) that it gives a true measurement of the hydrogen-ion concentration.

**Comparison of Results with those of Other Investigators of Antimony Electrodes.**—There have been a number of investigators who have worked with antimony–antimony oxide electrodes. The electrodes have

[19] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore Md., 1928, 3d ed.

been of three types: the metallic stick, the plated and the dropping electrode of Roberts and Fenwick. Shukov and Aveyevich[20] and Brinkman and Buytendiyk[21] used electrodes made by plating out antimony metal on a platinum electrode. All of the other investigators previously mentioned in this article used the stick metal electrode. This type of electrode has been favored because of its ease of preparation and applicability. A comparison of the results, as noted by the Nernst equation, arrived at by different investigators proves interesting. The potential of the antimony electrode against the normal calomel electrode is taken as the basis.

TABLE IV

COMPARISON OF RESULTS OF INVESTIGATORS WITH THE Sb | $Sb_2O_3$ ELECTRODE

| | |
|---|---|
| | Stick metal electrode |
| Franke and Willaman | $E = 0.050 + 0.054\ P_H$ |
| Lava and Hemedes[22] | $E = 0.052 + 0.057\ P_H$ |
| Kolthoff and Hartong | $E = 0.0415 + 0.0485\ P_H$ ($P_H$ 1–5) 14° |
| | $E = 0.009 + 0.0536\ P_H$ (above $P_H$ 9) 14° |
| Britton and Robinson | $E = 0.018 + 0.0534\ P_H$ (calcd. from curve) |
| Harrison and Vridhachalam | $E = 0.0234 + 0.0498\ P_H$ 30° |
| This investigation | $E = 0.030 + 0.05915\ P_H$ |
| | Plated electrode |
| Shukov and Aveyevich | $E = 0.009 + 0.053\ P_H$ |
| | Dropping electrode |
| Roberts and Fenwick | $E = 0.138 + 0.05915\ P_H$ |

With the stick metal electrodes all of the solutions were stirred with the exception of those of Harrison and Vridhachalam and the present investigation. It will be noted that in no case, with the stirred solutions, is the slope of the curve the correct theoretical value. The comparison of the $E_0$ value of Harrison and Vridhachalen and this investigation is noteworthy as both were obtained with unstirred solutions. The difference in temperature and the drawing of a line to meet all possible points in their investigation might account for the difference in the slope of their curve.

The difference in the $E_0$ value between the present investigation and that of Roberts and Fenwick may be explained by the difference in the nature of the electrode. They used a dropping electrode and were very careful to exclude all air in their closed electrode vessel, replacing it with nitrogen. Our electrode vessel was open to the air and the solution contained the normal amount of dissolved air at atmospheric conditions. Our experiments showed that the addition of more air to the solution lowers the potential, so it is reasonable to believe that a system with the air and

[20] Shukov and Aveyevich, *Z. Elecktrochem.*, **35**, 349 (1929).

[21] Brinkman and Buytendiyk, *Biochem. Z.*, **199**, 387 (1928).

[22] Lava and Hemedes, *Philippine Agr.*, **17**, 337 (1928).

oxygen excluded, as that of Roberts and Fenwick, will give higher potentials.


## Summary

1. The use of a vacuum-tube potentiometer with stick antimony electrodes eliminates drifting of the potential and gives rapid, constant and reproducible readings.

2. Stirring of a solution or the bubbling of a gas through it causes a deviation of the values away from the theoretical.

3. The stick antimony electrode in an unstirred solution in contact with air at equilibrium with both antimony and antimony trioxide gives a correct measurement of $P_H$ values from $P_H$ 2 to 7 inclusive. The value of $E$ with this electrode measured against the normal calomel electrode is obtained by the equation $E = +0.030 + 0.5915\ P_H$.


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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

# PHOTOMETRIC DETERMINATION OF THE SOLUBILITY OF SILVER CHLORIDE AND OF MERCUROUS CHLORIDE[1]

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## Introduction

Utilization of the Tyndall beam in the determination of the amount of suspended material in dispersed systems has often been attempted. As pointed out by Wells,[3] the phenomena encountered are extremely complex. Turbidity is doubtless a measure of other factors beside concentration. In spite of such limitations, methods employing the Tyndall beam possess certain attractive features, one of the most significant of which is that of extreme sensitivity.

Nephelometric analysis, employing the comparison of intensity of light reflected by a suspension of unknown concentration with that from a suspension of the same substance of known concentration, is a convenient method for the quantitative estimation of a solid phase in suspension. It is unsuited to the precise determination of solubility because of the necessity for the presence of a definite quantity of the solid phase in the standard.

Popoff and Neuman[4] appear to have been the first to utilize an optical method involving the estimation of the solubility of a sparingly soluble inorganic salt by noting the first appearance of the Tyndall beam in a

[1] For suggestion of the problem and for generous assistance in the earlier part of the work the authors are indebted to the late Stephen Popoff.

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[3] P. V. Wells, *Chem. Reviews*, **3**, 331–382 (1927).

[4] Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853–1860 (1930).

series of dilute solutions of suitable reactants under controlled conditions. The present investigation was undertaken for the purpose of establishing the sensitiveness and reliability of such a method and of developing a generalized technique by means of which the solubility of various inorganic precipitates could be measured.

## Purification of Materials and Preparation of Solutions

**Redistilled Water.**—Distilled water from the laboratory supply system was distilled from alkaline potassium permanganate solution in a specially constructed Pyrex glass still provided with a tin condenser tube attached to the still-head by means of a water seal. The Pyrex glass still-head was so constructed as to cause the vapor to reverse the direction of its course twice before entering the condenser, thus eliminating mechanical entrainment of impurities. Dust was excluded by a glass shield which fitted over the neck of the receiver. A portion of each new supply of water was tested in the tyndallmeter with an excess of silver nitrate to insure the absence of dissolved gases of an objectionable nature.

**Potassium Chloride.**—A good grade of C. P. potassium chloride was twice recrystallized from redistilled water, the hot concentrated solution being filtered through a good grade of filter paper in each case and finally through a glass filtering crucible with sintered glass bottom to remove shreds of filter paper. The recrystallized salt was collected in a similar filtering crucible.

**Silver Nitrate.**—C. P. silver nitrate, labeled as containing 0.002% of chloride, was used as the starting material. A solution formed by dissolving about 0.01 g. of the solid in a few cubic centimeters of redistilled water showed readily distinguishable opalescence when examined in the tyndallmeter. After two crystallizations from redistilled water a sample of the product yielded a solution which appeared free from opalescence as compared with pure water. The filtering technique was similar to that employed for potassium chloride with the exception that a crucible with sintered glass bottom was used for all filtrations.

**Mercurous Perchlorate.**—The mercurous perchlorate used in this investigation was prepared by Wirth and Ough as described in the article by them.[5] The stock solution of this salt was also prepared and analyzed by them as described in the same paper.

**Nitric Acid.**—C. P. nitric acid was purified by two distillations, rejecting the first and last portions and expelling the oxides of nitrogen, after which it was diluted with redistilled water. It was standardized indirectly against potassium acid phthalate by the use of carbonate-free sodium hydroxide solution.

**Perchloric Acid.**—70–72% perchloric acid, distilled in vacuum, was diluted with redistilled water and standardized, as in the case of nitric acid, against potassium acid phthalate.

The stock solutions of silver nitrate and of potassium chloride were approximately 0.1 molar. They were prepared by dissolving the moist recrystallized salts in redistilled water. They were analyzed both gravimetrically and by the Mohr titration method using weight burets.

The calculated weight of the stock solution, in the case of each salt, was diluted to two liters in a flask which had been calibrated in terms of a standard (calibrated) 50-cc. pipet. The resulting intermediate solution was diluted, by use of the calibrated pipet and flask, to a concentration of $2.608 \times 10^{-4}$ mole of salt per liter to form the experimental solutions. Equal volumes of the experimental solutions of the two salts were stoichiometrically equivalent. Assuming a value of $1.304 \times 10^{-4}$ mole per liter for the

[5] Popoff, Riddick, Wirth and Ough, THIS JOURNAL, **53**, 1195 (1931).

solubility of silver chloride, a mixture containing 5 cc. of each of the experimental solutions in sufficient water to make a total volume of 100 cc. should just initiate precipitation of silver chloride at a temperature of 25°.

The concentration of the experimental solution of potassium chloride used for determining the solubility of mercurous chloride was $2 \times 10^{-4}$ mole per liter. That of the mercurous perchlorate solution was $1 \times 10^{-4}$ mole per liter. Assuming the solubility of mercurous chloride to be $5 \times 10^{-6}$ mole per liter, a condition of incipient precipitation should be reached by mixing together 5 cc. of each of the experimental solutions with water in a total volume of 100 cc. at a temperature of 25°.

**Optical Instruments and Accessories.**—The tyndallmeter used in this investigation, and previously used by Popoff and Neuman,[6] is a modified form of the instrument used by Tolman and co-workers.[7]

A brass bottle-holder, blackened inside to eliminate reflection and provided with suitable openings, was designed and used by the authors.

The Gradation Photometer, or "Stupho," as originated by C. Pulfrich and manufactured by Carl Zeiss, Incorporated, was used in conjunction with the tyndallmeter.

Great difficulty was experienced in finding suitable containers for the suspensions; 100-cc. oil sample bottles of moulded glass, although fairly satisfactory in other respects, invariably caused contamination of the contents when agitated in the bath. Protection by application to the corks of melted paraffin, both externally and internally, failed to eliminate this difficulty. In fact, pieces of clean paraffin agitated with pure water for a period of an hour or more always caused turbidity, possibly due to the formation of an emulsion. Rubber stoppers, cleaned by the usual laboratory methods, were even less satisfactory. A minute quantity of foreign solid material, the presence of which might not adversely affect other methods, renders photometric measurements unreliable.

Cylindrical flat-bottomed bottles with rounded shoulders were fashioned to dimensions of about 3.2 × 20 cm. from heavy-walled *moulded* Pyrex tubes. The neck of a bottle was formed by sealing a piece of Pyrex tubing of 12 mm. diameter to the rounded shoulder. The volume of each bottle was about 125 cc., allowing sufficient free space to provide for thorough mixing of the contents when the bottles were laid in the bath and rocked about a horizontal axis perpendicular to the length of the bottle.

## Experimental Method

The method of determining the solubility of a substance consisted essentially of the examination in the tyndallmeter and in the gradation photometer of a series of sealed bottles containing mixtures of extremely dilute solutions of the reactants in water or in dilute acid. Equal volumes of the experimental solutions were always used. By successively increasing the amounts of the two reactants in a total volume of 100 cc., turbidity was caused in the more concentrated of a series of such solutions. The value for the solubility of the saturating phase was considered to be between the highest concentration which failed to show turbidity and the lowest concentration at which turbidity could be seen when the bottles were examined in the optical instruments.

To avoid the formation and consequent partial settling of a true precipitate, the solutions were added to the bottle in the following order:

[6] Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853–1860 (1930).

[7] Tolman and Vliet, THIS JOURNAL, **41**, 297 (1919).

one of the reactants, nearly all of the water (or the dilute acid if an acid was used), the other reactant, and finally the remainder of the water required to give a total volume of 100 cc.

After the bottles had been sealed in a blast lamp they were immersed in a constant temperature water-bath, maintained at a temperature of 25 ± 0.02°, in which they were agitated for a period of at least four hours. Results of tests covering periods of time up to seventy-two hours indicated no significant change between four and twenty-four hours in the case of barely perceptible turbidities. Longer periods of time caused opalescence and settling of the suspended particles in even the most dilute suspensions.

An attempt was made to approach equilibrium from both lower and higher temperatures. Cooling about 0.2° for one hour with subsequent shaking for four hours or longer at 25° produced no perceptible change in the results. Cooling in ice water for half an hour caused opalescence and settling of suspended particles. A suspension could not again be obtained after this treatment.

After the bottles were removed from the bath they were carefully wiped clean and dry before being placed in the optical instruments. The importance of having the bottles clean cannot be too strongly emphasized. Before immersion in the reservoir of the gradation photometer the bottles were rinsed with distilled water at room temperature to remove particles of lint or dust. The distilled water in the reservoir was changed frequently. The entrance of dust or other foreign material was carefully guarded against. Readings were made in a darkened room only after the eye of the observer had become accustomed to the subdued light

## Experimental Results and Discussion

TABLE I

SILVER CHLORIDE

| Molarity of $HNO_3$ | $S \times 10^5$ of AgCl | | Molarity of $HNO_3$ | $S \times 10^5$ of AgCl | |
|---|---|---|---|---|---|
| 0.0000 | 1.49 | 1.56 | 0.119 | 1.62 | |
| .0024 | 1.41 | 1.45 | .238 | 1.70 | |
| .0238 | 1.51 | 1.56 | .524 | 2.35 | 2.40 |

TABLE II

MERCUROUS CHLORIDE

| Molarity of $HClO_4$ | $S \times 10^6$ of $Hg_2Cl_2$ | Molarity of $HNO_3$ | $S \times 10^6$ of $Hg_2Cl_2$ |
|---|---|---|---|
| 0.0005 | 4.7 | 0.005 | 5.2 |
| .005 | 4.8 | .010 | 5.6 |
| .010 | 5.0 | .100 | 5.8 |
| .100 | 5.5 | | |
| .200 | 6.3 | | |

The $S$ in Tables I and II represents the solubility in moles per liter of the saturating phase at a temperature of 25°.

The value for the solubility of silver chloride in water at 25°, as recorded in the "International Critical Tables,"[8] is $1.304 \times 10^{-5}$ mole per liter. Pinkus and Berkolaïko,[9] using a method in which the final measurement of solubility was made with the aid of a nephelometer, found $1.42 \times 10^{-5}$. Popoff and Neuman,[4] also using an optical method, reported $1.278 \times 10^{-5}$.

Our values are somewhat higher than those obtained by others. The possibility of the existence of supersaturation was considered and precautions were taken to eliminate it. Solutions cooled to incipient turbidity and subsequently agitated at 25° for several hours failed to show any evidence of the presence of precipitated material in any concentration less than that originally required to show turbidity. Although a suspension could not again be obtained after this treatment, the presence of precipitated material could be easily detected in the more concentrated solutions by vigorously shaking the bottles, allowing them to stand undisturbed for one minute to allow entrapped air bubbles to escape, and then examining them in the tyndallmeter.

As indicated in Table I, the solubility of silver chloride evidently reaches a minimum in the presence of a very small quantity of nitric acid rather than in water containing only silver chloride and the exceedingly small quantity of potassium and nitrate ions from the reactants. The danger of error involved in extrapolation to zero concentration of a solvent electrolyte is thus strikingly shown.

Previous to 1904 the published values of the solubility of mercurous chloride varied from $1 \times 10^{-6}$ to $6 \times 10^{-6}$ mole per liter. Ley and Heimbucher,[10] using an electromotive force method, found $0.8 \times 10^{-6}$. Brodskii,[11] also using an electromotive force method, reported $1.15 \times 10^{-18}$ as the solubility product of mercurous chloride at 25° which would indicate a solubility of the order of $6.6 \times 10^{-7}$.

The sensitiveness of our method was ascertained by determining the smallest amounts of the reactants by which a non-turbid solution could be made to show turbidity. The amount of silver chloride required to produce a perceptible change was approximately $5 \times 10^{-7}$ mole per liter. The sensitiveness has therefore been stated as $\pm 2.5 \times 10^{-7}$ mole per liter. Likewise, the sensitiveness in the case of mercurous chloride is approximately $\pm 1 \times 10^{-7}$ mole per liter.

The precision attainable in photometric measurements is commonly assumed to be of the order of 0.5 to 0.2% under the most favorable conditions. The term "favorable conditions" includes uniformity of particle size in the suspended medium. Until the difficulty of obtaining even approximate uniformity of particle size by precipitation

[8] "International Critical Tables," 1929, Vol. VI, p. 256.

[9] Pinkus and Berkolaïko, *J. chim. phys.*, **27**, 364–385 (1930).

[10] Ley and Heimbucher, *Z. Elektrochem.*, **10**, 301–3 (1904).

[11] Brodskii, *ibid.*, **35**, 833 (1929).

methods can be at least minimized, it is probable that the photometric method cannot be made sufficiently sensitive to replace older methods of determining solubility. The present investigation has demonstrated, however, that experimental data secured by photometric measurements may serve as a valuable check on the accuracy of other methods. Obviously it cannot be used for very soluble substances, and probably not for extremely insoluble ones such as copper sulfide.

The experimental work is tedious. It is extremely difficult, under ordinary working conditions, to exclude completely dust and traces of stopcock grease from the solutions while they are being transferred, and to prevent contamination by traces of hydrogen chloride, ammonia and other undesirable gases from adjacent laboratories. In view of these and other limitations the method cannot be said to be of general applicability in its present stage of development.

Some interesting observations were made during attempts to stabilize suspensions of inorganic salts by means of protective colloids. The results are not included here because of the uncertainties involved in any interpretation of solubility data obtained in the presence of a stabilizing agent.

The junior author was indebted to Associate Professor Stephen Popoff, Head of the Analytical Division, Department of Chemistry and Chemical Engineering, State University of Iowa, for suggesting the problem in photometry and for his assistance in the earlier part of the work. The authors, however, assume responsibility for this report, the major portion of which is based on research done after Dr. Popoff was obliged because of prolonged illness to relinquish supervision of the work.

## Summary

1. An improved technique for the photometric determination of the solubility of sparingly soluble salts has been developed, employing a modified tyndallmeter and a gradation photometer to detect the appearance of turbidity in the solutions.

2. The solubility of silver chloride in five concentrations of nitric acid and in water containing potassium and nitrate ions from the reactants which produced the silver chloride was measured at 25°. The solubility in water was found to be between 1.49 and 1.56 $\times 10^{-5}$ mole per liter. The solubility was found to vary from 1.43 $\times 10^{-5}$ in 0.0024 molar nitric acid to 2.37 $\times 10^{-5}$ in 0.524 molar nitric acid.

3. The solubility of mercurous chloride in five concentrations of perchloric acid and in three concentrations of nitric acid was measured at 25°. It was found to vary from 4.7 $\times 10^{-6}$ mole per liter in 0.0005 molar perchloric acid to 6.3 $\times 10^{-6}$ in 0.200 molar perchloric acid; and from 5.2 $\times 10^{-6}$ in 0.005 molar nitric acid to 5.8 $\times 10^{-6}$ in 0.100 molar nitric acid.

4. The sensitiveness of the method is of the order of $\pm 2.5 \times 10^{-7}$ mole per liter for silver chloride in nitric acid of concentrations from 0.0024 to 0.240 *M*. In the case of mercurous chloride the sensitiveness is of the order of $\pm 1 \times 10^{-7}$ mole per liter.

IOWA CITY, IOWA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 301]

# THE HEAT OF IMMERSION OF SILICA GEL IN VARIOUS PETROLEUM SUBSTANCES

BY RICHARD W. STENZEL

RECEIVED AUGUST 29, 1931 PUBLISHED MARCH 5, 1932

In a study of the retention of crude oils by sands, it becomes of interest to know what particular kinds of petroleum substances are most likely to resist removal by the ordinary production methods. As a starting point for laboratory investigations, the oil sands may be considered as agglomerates of fine grains under pressure, a picture which is probably not oversimplified. Such a porous structure has, of course, capillary properties and undoubtedly will give rise to selective adsorption phenomena. It is the purpose of this paper to consider a means of arriving at some quantitative conclusions regarding such adsorption processes. For the sake of further simplicity the following considerations will be limited to silica–oil systems.

In order to determine the capillary characteristics of the various petroleum constituents, their selective adsorption might conceivably be directly measured. However, the experimental difficulties are considerable, and a simpler method was sought. The one decided upon was the measurement of the "heat of wetting," better called the heat of immersion, that is, the heat evolved when silica is brought into contact with an excess of a petroleum substance. It was thought that this heat effect might give an insight into the relative adsorption tendencies of such substances. While such values cannot be directly applied to adsorption equations such as that of Gibbs, the complexity of systems such as crude oils and their sands precludes at present such thermodynamic treatment, and more than a prediction of the relative adsorption tendencies can hardly be expected.

The literature contains comparatively few data on the heats of immersion of solids in hydrocarbons. Parks[1] has given results on the heats of immersion of silica and silica gel in water and has estimated the heat evolved per unit area, but considering the experimental procedure the values are probably far from accurate. Gaudechon[2] has made some determinations on the heats of immersion of a silica "dite amorphe" in various liquids, including pentane and hexane. No information is given as to the methods of the experiment, so that these data are also of uncertain value. Recently Grimm, Raudenbusch and Wolff[3] have measured

[1] Parks, *Phil. Mag.*, [6] **4**, 240 (1902).

[2] Gaudechon, *Compt. rend.*, **157**, 209 (1913).

[3] Grimm, Raudenbusch and Wolff, *Z. angew. Chem.*, **41**, 105 (1928).

the heats of immersion of silica gel in a number of substances in connection with their investigation of the fractionation of binary mixtures with the aid of silica gel. Bartell and Ying Fu[4] have made similar measurements using both a "dehydrated" and a hydrated silica gel. Harkins and Dahlstrom[5] have measured the heats of immersion of pigments in a number of liquids and have confirmed the observations of Grimm, Raudenbusch and Wolff that great care in removing polar substances from the organic liquids is necessary in order to obtain reliable results. The necessity for such precautions seems to have escaped the earlier workers. The results of these investigations will be discussed later. It is pertinent to note, however, that the various heat effects obtained by different authors show poor agreement even in the relative values.

Bartell and Miller[6] have developed a method for obtaining "adhesion tensions" of silica with various liquids which appears promising but evidently requires further extension to establish the thermodynamic relationships involved.

## I. Preliminary Investigations

During the preliminary work it was thought desirable to determine the heat of immersion of finely ground quartz, which would allow an estimate of surface area to be made. However, the heat effects, though positive, were discouragingly small, even when large amounts of the powder were mixed with just sufficient oil for thorough wetting. For a silica which passed a 200-mesh sieve and had been dried in a current of dry air at 1000° for several hours, these heat effects were of the order of 0.05 calorie per gram, corresponding to less than $10^{-4}$ calories per square centimeter. This is about one-tenth the effect obtained by Parks[1] for the heat of immersion of silica in water. Koehler and Mathews[7] found no net heat effect at all when they immersed finely divided lead sulfate in a saturated lead sulfate solution, even with areas as large as 32,000 sq. cm./g. It was obvious then that in order to measure a heat effect with powdered silica, the ordinary calorimetric methods would need to be considerably modified.

The use of powdered silica being thus found inadvisable, silica gel was used instead. The most recent views as to the nature of this material are that it is essentially an aggregate of capillary pores, offering a large surface per unit weight.[8] As a first step, then, it was decided to study the heat of immersion of silica gel in various petroleum substances.

## II. Apparatus and Materials

**1. Calorimeter.**—The method of calorimetry was similar to that used by Patrick and Grimm.[9] The calorimeter consisted of a 100-cc. vacuum-walled flask over which was fitted a hard rubber cover. In this cover were mounted a Beckmann thermometer, a nichrome wire heater, and a copper stirrup which served at once as a stirrer and as a holder for the glass bulbs in which the silica gel had been sealed. The glass bulbs were broken by means of a rod to the end of which was fastened a four-pointed "tooth."

[4] Bartell and Ying Fu, "Colloid Symposium Annual," 1929, Vol. VII, p. 135.

[5] Harkins and Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930).

[6] Bartell and Miller, *ibid.*, **20**, 738 (1928).

[7] Koehler and Mathews, THIS JOURNAL, **46**, 1158 (1924).

[8] Patrick, "Colloid Symposium Annual," 1929, Vol. VII, p. 129.

[9] Patrick and Grimm, THIS JOURNAL, **43**, 2144 (1921).

The bulbs could thus be broken beneath the surface of the liquid, which was considered essential since it was found that exposure of the gel to the vapors for an appreciable length of time changed the heat effect considerably. The heater had a resistance of 1.64 ohms, and was connected to a number of dry cells in parallel. The vacuum flask required a charge of only 35 cc. of oil and it was found that intermittent manual stirring was sufficient to keep the temperature equalized. Repeated calibration using a measured heat input through the nichrome coil showed that the reproducibility of the calorimetric technique was well within 0.1 cal. and thus within the experimental error as shown below.

Since the metallic parts of the apparatus would be attacked by the mercaptan sample, the copper cradle and breaker rod were replaced by glass and the nichrome heating coil immersed in a thin-walled glass tube filled with oil when that substance was used.

**2. Silica Gel.**—This was a commercial silica gel powder which was purified by repeated washings with hydrochloric acid and finally with distilled water until free from chlorides. It was then air dried and sifted through a 40-mesh screen. The extremely fine particles had, of course, been removed by the decantation process so that only the grainy material was left. This was then placed in a furnace and dried for three to four hours in a current of air (dried by phosphorus pentoxide) at a temperature of 250–300°. About 500 g. of the material was prepared in this way, 50 g. at a time; then all of it was placed in a large bottle, thoroughly mixed by shaking, and then distributed to ten 100-cc. flasks which were tightly stoppered and placed in a cabinet containing silica gel as a desiccator. This cabinet was so arranged that the gel could be transferred from the flasks to the glass bulbs without exposure to the laboratory atmosphere. In this way it is believed that the charges used in the experiments were very nearly identical in composition.

An analysis of the gel showed a water content of 4.5% and impurities 0.075%. The latter are not considered of significance for the purposes of these experiments.

**3. Hydrocarbons.**—The samples of benzene, *n*-hexane, *n*-decane, cyclohexane and *n*-butyl mercaptan were all C. P. products from the Eastman Kodak Laboratories. All but the last were redistilled and the fractions used had a boiling range of about half a degree.

## III. Experimental Procedure and Results

In making the heat of immersion determinations, about 0.7 g. of the silica gel was transferred to the previously weighed glass bulbs in the atmosphere of the desiccated cabinet, then the neck of the bulb was sealed off and the final weight obtained. The bulb was then placed in the cradle, the cover of the calorimeter put into place, the thermometer inserted and the whole placed in an air-bath, the temperature of which was automatically regulated to within 0.1° at about 29.5°. Since the temperature coefficient of the heat of immersion is probably nearly equal to zero[10] the values obtained will be valid for a considerable range above and below this temperature.

After the apparatus had been in the air-bath for one hour, the calorimeter temperature was about 2 degrees below that of the bath. Temperature readings were now recorded, and after about thirty minutes the glass bulb was broken. The temperature rise was usually about 0.5°, and the readings were continued until temperature equilibrium had again been established. Then the heater was turned on and a quantity of heat approximately equal to that developed by the silica gel was introduced. By plotting the temperature–time curves, the actual temperature rise could be determined and from this could be calculated the heat capacity of the apparatus and the heat of immersion of the gel in the liquid. Previous calibration had shown that a simple graphical method could be employed which would give the true temperature differences.

[10] *Cf.* Brown and Mathews, "Colloid Chemistry," 1926, p. 457, Alexander ed.

Such an empirical method was necessary since the usual heat loss formulas are hardly applicable to a vacuum flask type of calorimeter. This method of determining the heat capacity of each charge eliminated any uncertainties which would be introduced by the use of calculated heat capacities. It should be mentioned that the dry cells were short-circuited for about a minute through a resistance equal to that of the calorimeter heater before the latter was turned on, so that no fluctuation of the current would occur due to polarization. A typical set of data is tabulated below:

Sample: *n*-decane; silica gel, 0.8384 g.

Heat capacity

| | | | |
|---|---|---|---|
| Amps. | 0.835 | Final temp. | 2.604 |
| Sec. | 25.4 | Initial temp. | 2.311 |
| Calories | 6.96 | Temp. rise | 0.293° |

Heat Capacity = 6.96/0.293 = 23.8 cal./°C.

Heat of immersion

| | |
|---|---|
| Final temp. | 2.192 |
| Initial temp. | 1.916 |
| Temp. rise | 0.276° |

Heat of immersion = (0.276)(23.8)/0.838 = 7.84 cal./g.

Preliminary determinations confirmed the observations of Grimm, Raudenbusch and Wolff[3] and of Harkins and Dahlstrom[5] that minute quantities of foreign substances, especially water, in the organic liquids greatly affected the heats evolved. This is illustrated by the following table, in which the heats of immersion of the undried substances are compared with the final values of the dried substances.

EFFECT OF DRYING ON THE HEAT OF IMMERSION

| Substance | Heat of immersion (cal./g.) Undried | Dry |
|---|---|---|
| Water | 25.4 | |
| Benzene | 17.4 | 13.1 |
| Hexane | 16.6 | 7.9 |

Thus it became necessary to find means of effectively drying the liquids. Benzene was thoroughly dried by sodium shavings and redistilled in an atmosphere of air dried with phosphorus pentoxide. It was then transferred without contact with the laboratory atmosphere to the calorimeter, which had previously also been dried by passage through it of dry air for several hours. The heat of immersion thus obtained was 13.0 and 13.2 cal./g. for two consecutive runs.

Another method was then tried in which the benzene without previous drying was placed in the calorimeter, then 4 g. of silica gel added and the mixture allowed to stand for about two hours to attain equilibrium. The heat of immersion was now determined as before, and the values 13.1 and 13.0 cal./g. obtained. These results show that careful drying by sodium or silica gel gave the same values, which is in accord with the experience of Grimm and co-workers mentioned above. Since drying by means of a preliminary charge of silica gel was more convenient, and since it would remove other incidental impurities besides water, this method was used in the remainder of the determinations.

The accuracy of the method is thus dependent on two main factors, providing the calorimetric technique is adequate. One is the reproducibility of the samples of the solid used. Most of the previous workers have activated each sample separately, which introduces the possibility of a variation that was avoided in this work by activating be-

forehand all the gel required. The other is the effectiveness of the drying procedure. It was found that as successively larger quantities of the dehydrating charge (of silica gel) were used, the heat effects reached a limiting minimum value. Thus when 1 g. of the gel was used as the dehydrant, the heat effect was lower than with an undried sample but not yet at the lowest value. When more than 2 g. was used, the final limiting value was obtained, and these were reproducible within 0.2–0.3 cal./g. The heat effect due to the breaking of the glass bulbs was determined and found to be somewhat less than 0.1 cal. but could not, of course, be corrected for.

Thus it can be seen that the calorimetric procedure is of secondary importance compared to the necessity of ridding the liquid of the last traces of impurities. It is believed that the preliminary wetting with silica gel accomplished this conveniently and quite thoroughly.

The final values thus obtained are given in the first column of Table I. Comparison of these values with those of other authors is not directly possible because the magnitudes of the heats of immersion appear to be functions both of the water content of the gel and of its method of preparation. This would lead to the conclusion that heat of immersion data on silica gel are valueless except for the specific gel under consideration. However, it is now evident that one of the principal reasons for the decided disparity in such values is the remarkable effect which even traces of water in the liquid used have upon the heat of immersion. Of the values on silica gel published to date, only those of Grimm, Raudenbusch and Wolff[3] seem to have been obtained with due precautions against contamination by moisture.

TABLE I

HEAT OF IMMERSION OF SILICA GEL IN VARIOUS SUBSTANCES

(Calories per Gram of Gel)

| | Observed values | | | | | | Values relative to water and benzene | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Grimm R. & W. | | | Bartell and Ying Fu | | | Grimm R. & W. | | "$q$" for water |
| Substance | This paper | wide pores | narrow pores | Patrick *et al.* | "dry" hydr. | | This paper | wide pores | narrow pores | interface ergs |
| Cyclohexane | 6.5 | 3.6 | 6.2 | | | | 5.0 | 5.5 | 5.5 | |
| *n*-Hexane | 7.9 | 3.6 | 6.5 | | | | 6.0 | 5.5 | 5.7 | 58.6 |
| *n*-Decane | 7.8 | | | | | | 6.0 | | | |
| Carbon tetrachloride | | 4.7 | 7.3 | 8.4 | 10.0 | | | 7.2 | 6.5 | 43.3 |
| Chloroform | | 6.2 | 10.9 | | 14.5 | | | 9.5 | 9.6 | |
| Toluene | | 6.4 | 11.3 | | | | | 9.8 | 10.0 | |
| Benzene | 13.1 | 6.5 | 11.3 | 11.1 | 12.7 | 21.5 | (10.0) | (10.0) | (10.0) | 65.0 |
| Water | 25.4 | 14.6 | 20.9 | 19.2 | 15.9 | 24.3 | (20.0) | (20.0) | (20.0) | 117.0 |
| Ethyl alcohol | | 12.8 | 23.7 | 22.6 | 16.6 | 26.9 | | 17.5 | 22.7 | |
| Methyl alcohol | | 13.4 | 22.9 | | | | | 18.4 | 21.9 | |
| *n*-Butyl mercaptan | 25.9 | | | | | | 20.4 | | | |

Table I gives the important values of the heats of immersion of silica gel in various liquids. The values of Parks and of Gaudechon[2] are not given because of their uncertainty. The first three columns of the table show the values obtained by the above authors and those of this paper. One of their gels was designated as "wide-pored," the other as "narrow-pored," the difference evidently being determined by the apparent density of the gels. As can be seen from the table, there is no

agreement in the absolute values among any of the gels used. However, there does seem to be possible a general classification in each group, on the one hand of the non-polar liquids like hexane and benzene, and on the other of water and other polar liquids. The former show low heat effects, the latter high ones. This suggests a correlation with dielectric constants, molecular volumes, etc., but none of these appear to be fruitful in indicating the direct cause of the difference in the heat effects.

Upon analyzing the data, it was found that the non-polar, water-insoluble liquids could be compared by using, say, benzene as a standard and computing the relative values for the others. Thus the heat effect for benzene and a hypothetical gel may be chosen as 10 cal./g., and if the actual gels are considered to differ merely in specific surface, the heat effects for the other substances may be converted to relative values for the hypothetical gel. The results are shown in the table, and bring the values for the three different gels into fairly good agreement. This is believed to be the first instance in which differently prepared samples of silica gel have been found to give comparable values, and the reason is to be found undoubtedly in the precautions used to insure removal of the last traces of water and similar impurities.

In a similar way, water may be assigned a value of 20 cal./g. and the water-like substances compared on this basis. The author did not study the alcohols, so that no comparison of the values for this class of substances can be made.

## IV. Discussion

The cause of the heat effect attending the immersion of a solid in a liquid is usually considered to be the replacement of the solid surface by a solid–liquid interface. Since the interfacial energy cannot be measured, only the difference between the two total energies is determined by the heat effect. On the hypothesis that the thermodynamics of plane surfaces can be applied to such substances as silica gel, Bartell and Ying Fu[4] have attempted to calculate the free energies of immersion from the heat effects. This involves an assumption of the independence of temperature of $k$ in the equation $\sigma_1 - \sigma_{12} = k\sigma_2$ where $\sigma_1$ and $\sigma_2$ are the surface tensions of the solid and the liquid, and $\sigma_{12}$ is their interfacial tension. This cannot be tested for solid–liquid interfaces, but for interfaces such as water–organic liquid, $k$ is found to vary with the temperature, so that it is hardly safe to assume it to be constant for the former.

An analogy which suggests itself and which was made use of by Harkins and Dahlstrom[5] is the comparison of the heat of immersion of silica gel with a hypothetical heat of immersion of water in the same liquids. Thus if it is considered that drops of water of 1 sq. cm. surface area are immersed in an organic liquid having an interfacial tension of $\sigma_i$ against water, the total heat evolved would be the difference between the total

energy of the water surface before immersion and the total energy of the interface after immersion. This can be expressed as

$$\text{Heat evolved} = q = E_{\text{water}} - E_{\text{interface}}$$

But the total energy of the interface is given by

$$E_{\text{interface}} = \sigma_i - T\frac{d\sigma_i}{dT}$$

and the total surface energy of water at 25° is 117.0 ergs/sq. cm., so that

$$q = 117.0 - \sigma_i + T\frac{d\sigma_i}{dT}$$

These values have been calculated for those liquids for which the temperature coefficients of the interfacial tensions are available and are given in the column headed "$q$." While there is a similarity in the relative values, it is not sufficiently quantitative to warrant the conclusion that the two surfaces are alike in their behavior toward organic liquids. The Harkins and Dahlstrom data show similar trends.

For the present, then, the energies of immersion must be relied upon to give the best indication of the capillary characteristics of porous and finely divided substances toward the various liquids.

This work was carried on as a part of American Petroleum Institute Project 37, with funds made available by John D. Rockefeller and the Universal Oil Products Company. Grateful acknowledgment is made for this assistance and to Professors W. N. Lacey and R. M. Badger for their interest and helpful criticism.

## V. Conclusions

1. The heats of immersion of silica gel in various substances have been determined.

2. A method of correlation of heats of immersion of silica gel has been suggested, and the results of this paper have been found to agree with those of previous workers representing three differently prepared samples of silica gel.

3. The results indicate that the hydrocarbons investigated may be divided into three general groups. The paraffin and naphthene hydrocarbons, giving low heats of immersion; the aromatics, giving intermediate values; and the alcohols and sulfur compounds, showing high capillary activity not greatly different from that of water itself.

4. It is suggested that since at present the free energy changes attending the immersion of porous and finely divided solids cannot be determined, the heats of immersion furnish the best indication of the capillary characteristics of such solids.

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# IMPROVED APPARATUS FOR MICRO-ELECTROANALYSIS[1]

BY BEVERLY L. CLARKE AND H. W. HERMANCE

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Two related problems which frequently arise in chemical analysis are (1) the separation, identification and determination of small quantities of metallic ions where the volume of the liquid sample may be limited, and (2) where the volume is large relative to the metal concentration and cannot be reduced owing to high salt concentration. Both these problems are efficiently handled by electroanalytical methods, provided that micro-technique is suitably applied.

These problems have been attacked by others along similar lines.[2] The most widely used cell for micro-electroanalysis is that of Pregl.[3] The usefulness of this cell is somewhat limited by the employment of boiling for effecting agitation, and none of the other apparatus published is free from one or more of the following objections: (1) long time required for complete deposition; (2) structural fragility; (3) disparity in size and shape between electrodes, preventing simultaneous cathodic and anodic deposition; (4) absence of provision for agitation, or use of objectionable methods; (5) difficulty in washing electrodes.

The present paper describes two cells, for the respective purposes stated, in which these objectionable features are eliminated or minimized.

## Apparatus

**The Cell for Small Volumes.**—The large outer vessel (Fig. 1), sealed to the electrode compartment at its base, is a water-jacket which can be heated by a micro-flame. Figure 2-I shows the glass frame which in the assembled cell fits inside the electrode vessel and serves to support both the electrodes and the pumping device. Its lower end is flared to form a conical bell having a diameter about 4 mm. less than that of the container. While the two electrodes are held very close together, they cannot make contact or become fouled by touching the glass wall of the container. The support permits a free circulation of the electrolyte. This circulation is accomplished by the tube shown in Fig. 2-II, which is held erect in the axis of the cell. A stream of bubbles of air or of an inert gas is introduced by means of this tube into the space under the bell and causes a continuous overflow of liquid over the top of the tube A that supports the inner electrode. At the same time the suction caused by the removal of the liquid from under the bell further assists circulation in this direction by drawing upon that portion of the electrolyte in the space between the outer electrode and the wall of the containing vessel. A rapid agitation is thus maintained whereby

[1] Presented before the Physical and Inorganic Division, American Chemical Society, Buffalo, N. Y., Aug. 31–Sept. 3, 1931.

[2] Classen, "Quantitative Analyse durch Elektrolyse," 7th ed., Julius Springer, Berlin, 1927; Heinze, *Z. angew. Chem.*, **27**, 237 (1914); Riesenfeld and Möller, *Z. Elektrochem.*, **21**, 137 (1915); Brenneis, *Mikrochemie*, **9**, 385 (1931).

[3] Pregl, "Quantitative Organic Microanalysis," 2d ed., translated by Fyleman, P. Blakiston's Sons, Philadelphia, 1930.

the whole of the electrolyte is forced through the inter-electrode space several times a minute.

The electrodes are two platinum gauze cylinders 15 mm. high, the one having an inside diameter of 9 mm., the other, 18 mm., weighing 0.8 g., and 1.5 g., respectively.

**The Cell for Large Volumes.**—This cell is designed for the separation of small quantities of metals from large volumes of solution, when concentration of the sample is undesirable. Provision is made for the continuous and rapid circulation of the large liquid volume through the space between the micro-electrodes.

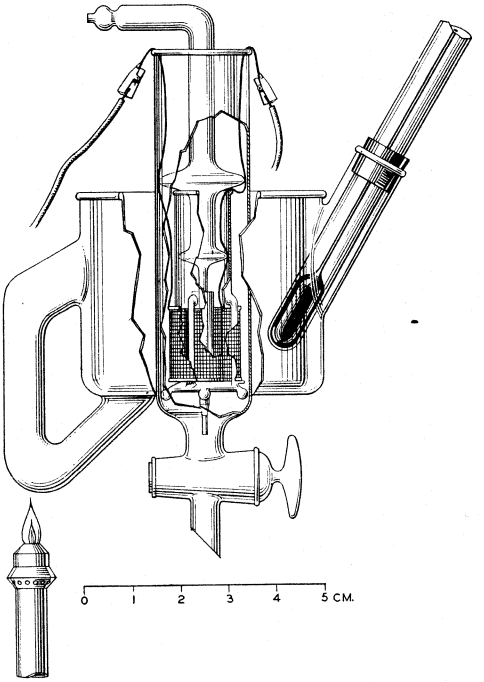


Fig. 1.—General view of cell for small volumes.

Figure 3 shows the cell container and accessory parts, and details of construction and assembly are given in Fig. 4. The size of the large reservoir B should accord with the volume of liquid to be electrolyzed. Within the tube C in Fig. 3 four internal glass projections, as shown in cross-section in Fig. 4-I, provide support at D for the tube E (Fig. 4-II), which in turn holds the inner electrode in position and includes a device for washing the deposit (see Experimental Section). Circulation of the electrolyte is effected by an air-pump similar to that used for the small cell. The small clearance between E and the tube C, and the crowding of the electrodes into this space, cause the velocity of flow through the inter-electrode space to be relatively great, thus accelerating the electrolysis. The bulb F above the electrode space serves to affect turbulent flow, as indicated by the arrows in Fig. 4-I, and thereby to bring about a desirable increase in agitation at this point. The stopper H is notched parallel to its axis to permit the escape of the air used for pumping.

The outer electrode (J in Fig. 4-II) is a cylinder of perforated platinum sheet or heavy gauze and is permanently fixed in place, snugly against the wall of the electrode chamber, by a stout platinum wire welded to the electrode and fused through the glass wall. The inner electrode (L in Fig. 4-II) is of platinum gauze, similar to that used for the small cell, and that portion of the lead wire in contact with the solution is enclosed in glass. The central electrode fits over the tube E with a clearance of about 0.5 mm. The clearance between the electrodes is 3 to 4 mm. In order to permit the removal of the inner electrode from the cell without interrupting the current, it is convenient to connect the platinum lead wire to the binding post by a short length of flexible tinsel cord with a small spring clip.

When the quantity of the ion in question is extraordinarily small and it is desired merely to effect a separation, the weighable electrode just described is conveniently replaced by that shown in Fig. 4-III. The deposit may then be dissolved in a drop of acid and subjected to microscopic identification tests or colorimetric estimation.

On account of its small active area, this disk electrode is particularly useful for the concentration of such small quantities as might escape observation when deposited on the larger cylindrical electrode.

**Manipulation.**—Successful practice of microchemical technique requires an almost meticulous attention to manipulative detail. It is therefore necessary to give somewhat elaborate descriptions of those manipulations involved in the operation of these cells that are not obvious from the drawings.

**Electrodes.**—The electrodes are first cleaned by immersion in hot, concentrated nitric acid, followed by rinsing with distilled water. They are next heated to dull redness in the oxidizing portion of a small Bunsen flame, then cooled and weighed on the Kuhlmann microbalance.[4] The electrodes should of course always be handled with suitable forceps.

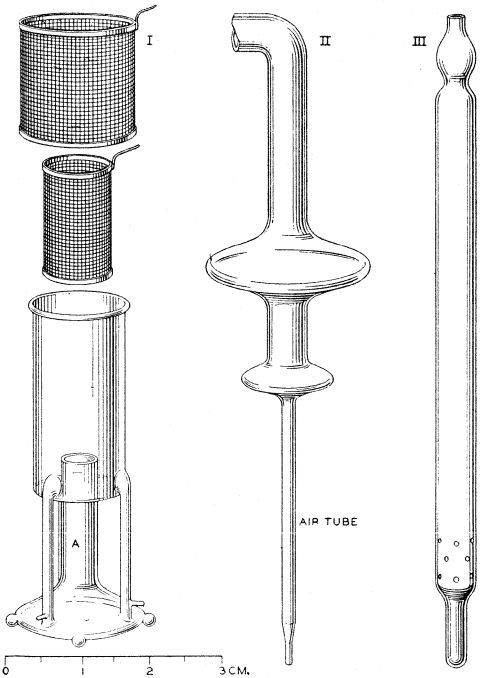

Fig. 2.—Detail of cell for small volumes.

### Assembly of the Cells

**(a) Cell for Small Volumes.**—After the electrodes have been weighed and assembled (Fig. 2-I), the unit is lowered into the cell vessel containing the solution to be electrolyzed, the volume of which is then so adjusted that its level coincides with the upper end of the tube A in Fig. 2-I. The air tube is now introduced as indicated, and bubbles admitted at such a rate that the liquid may be seen to flow regularly over the top of the tube A. Too much air should, of course, be avoided, since it may cause excessive spraying of the electrolyte. When the electrical connections are made, the apparatus is now ready for the electrolysis.

**(b) Cell for Large Volumes.**—The volume of the solution to be

[4] For very precise work Riesenfeld and Möller[2] have suggested a preliminary electrolysis of pure, dilute nitric acid for the purpose of stabilizing the weights of the electrodes by saturating them with hydrogen and oxygen, respectively, before weighing. Our experience, however, has indicated that the errors from this source are generally below those of weighings made on microbalance of the Kuhlmann type, and may therefore be disregarded.

electrolyzed is so adjusted that its level is a few mm. below the upper end of the inclined overflow tube N (Fig. 3). When the cylindrical electrode is used, the assembly is made as indicated in Fig. 4-I. When it is desired to use the small disk electrode, the stopper bearing the assembly (Fig. 4-III) replaces the stopper H used with the cylindrical electrode. The height of the sleeve D (Fig. 4-III) is adjusted in the stopper so that the disk is supported centrally in the space enclosed by the fixed, outer electrode. Insertion of the air-pump device completes the assembly.

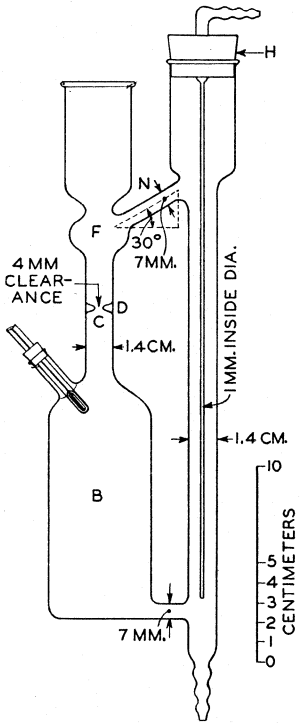


Fig. 3.—Cell for large volumes.

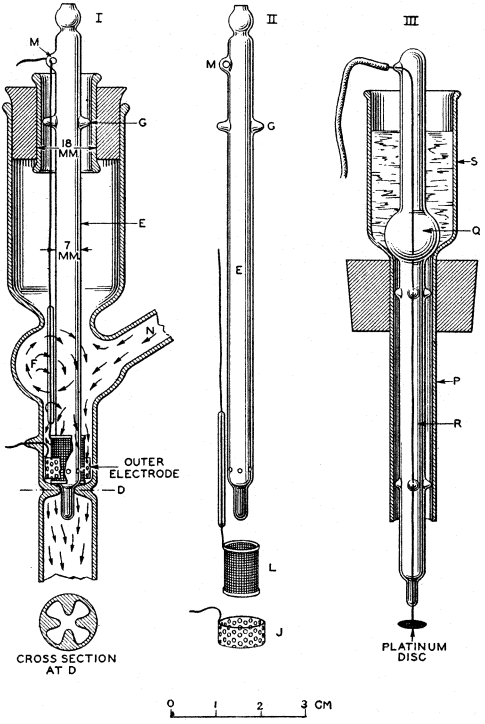


Fig. 4.—Detail of cell for large volumes.

**Washing the Electrodes.**—The importance of the careful and thorough washing of the electrodes cannot be too greatly emphasized. One reason for this is that, on account of the thinness of the layer of the deposited metal, it is in most cases essential to remove the electrolyte and wash the electrodes simultaneously and without interrupting the current, in order to prevent re-solution of the deposit. In the small cell, the simplest and most effective way of doing this is to drain the electrolyte from the cell by means of the stopcock at the bottom, while at the same time admitting distilled water from the top, the circuit remaining closed during the operation. When the complete displacement of the electrolyte is indicated by

the fall of the current to a negligible value, the electrodes may be safely removed.

If the excessive dilution of the electrolyzed solution involved in this method is objectionable, the following arrangement may be used. The device shown in Fig. 2-III, which minimizes the quantity of wash water when only the inner electrode is to be weighed, consists of a glass tube, of outside diameter slightly less than the diameter of the electrode. The lower end terminates in a short, solid process which fits loosely into the central overflow tube A. For a distance of 1 cm. from the end, the walls of the tube are perforated by a number of small holes. The open end of this tube is connected, by rubber tubing, to a reservoir containing distilled water, the flow being controlled by a suitable pinchcock. At the completion of the electrolysis, the air tube is withdrawn from the cell and this special washing tube inserted. The cell is drained slowly, while the wash water is admitted at the same rate through the perforations. At the same time, and without interrupting the current, the electrode is drawn up over the tube A until it occupies a position level with the perforations on the washing tube. The electrode, held in this position, is withdrawn together with the washing tube from the electrolyte: at the time it is pulled through the liquid surface it is surrounded by nearly pure wash water. If the holes in the washing tube are sufficiently fine, and these indicated operations are executed rapidly and skilfully, the electrolyte suffers a minimum amount of dilution.

In the large cell, the central supporting tube which holds the electrode in position has a perforated lower wall similar to that just described, and the technique of washing is identical with that used in the small cell. When the small disk electrode is used, however, another washing arrangement is employed. Before beginning the washing the cup S (Fig. 4-III) is filled with water which is held in place by the bulb Q ground into S. When the electrode is withdrawn, the water is released and trickles down through the meshes of the disk as the latter moves upward.

After removal from the cell, the deposits are further washed with redistilled alcohol and ether and dried for two to five minutes in an oven at 90°. They are then protected in stoppered test-tubes until weighed.

## Experimental

Many uses for these cells will suggest themselves. A few typical examples will be given in which the two cells, singly or in conjunction, enable the microanalyst to carry out difficult determinations with precision and expedition.

**Traces of Zinc in Aluminum Solutions.**—To 250-cc. portions of solutions of zinc sulfate and aluminum sulfate of the indicated compositions, was added enough potassium hydroxide to redissolve the aluminum hy-

droxide and furnish about 5% in excess. The solutions were electrolyzed in the large cell at room temperature for four hours, under 3.5 volts. Since the purest reagents that could be obtained for preparing these synthetic solutions contained considerable amounts of iron, the deposited zinc was contaminated with this metal, causing a dark appearance and a spongy texture. In order to purify the deposit it was redissolved and the iron precipitated as the hydroxide between *P*H 4 and 5. The zinc was then replated from the filtrate on a coppered electrode in the *small* cell.

TABLE I

DETERMINATION OF TRACES OF ZINC IN ALUMINUM SOLUTIONS

| Aluminum present, mg. | Zinc present, mg. | Zinc found, mg. | Error, parts per thousand |
|---|---|---|---|
| 5000.0 | 1.000 | 1.012 | +12 |
| 5000.0 | 0.500 | 0.483 | −34 |
| 5000.0 | .200 | .193 | −35 |
| 5000.0 | .100 | .099 | −10 |
| | | Average | ±23[5] |

A practical application of this procedure occurs in the analysis of aluminum-base die-cast alloys having very low (about 0.01%) zinc contents. Preliminary results indicate the superiority of this method over the sulfide separation.

## Separation of Small Quantities of Lead Present as an Impurity

(a) **Lead from Zinc.**—The data in Table II were obtained on 250-cc. portions of zinc sulfate–lead nitrate solutions of the indicated compositions, to each of which were added nitric acid to 2% and 25 mg. of copper sulfate, the latter functioning as a depolarizer which increases the hydrogen overvoltage and prevents the cathodic reduction of quadrivalent lead (Classen,[2] p. 226). Electrolysis was carried out at 60–70° for three hours at a potential difference of 2.8 volts. The final determination of the plated lead was made volumetrically as recommended by Lucas and Grassner.[6]

TABLE II

DETERMINATION OF TRACES OF LEAD IN ZINC SULFATE

| Zinc present, mg. | Lead present, mg. | Lead found, mg. | Error, parts per thousand |
|---|---|---|---|
| 10000.0 | 0.500 | 0.502 | + 4 |
| 10000.0 | .200 | .195 | −25 |
| 10000.0 | .100 | .096 | −40 |
| | | Average | ±23 |

[5] The precisions reported in Tables I to V, inclusive, are not to be regarded as representing the best that can be obtained: these data are presented merely as illustrations of types of separation to which the cells are applicable.

[6] Lucas and Grassner, *Mikrochemie*, Emich Festschrift, 199 (1930).

(b) **Lead from Nickel.**—The experimental procedure and conditions were similar to those in (a), except that the nickel was present as the C. P. nitrate. Table III shows the results.

TABLE III

DETERMINATION OF TRACES OF LEAD IN NICKEL NITRATE

| Nickel present, mg. | Lead present, mg. | Lead found, mg. | Error, parts per thousand |
|---|---|---|---|
| 5000.0 | 0.500 | 0.495 | −10 |
| 5000.0 | .200 | .196 | −20 |
| 5000.0 | .100 | .092 | −80 |
| | | Average | −37 |

Similar results were obtained for traces of lead in aluminum solutions.

## Separation of Small Quantities of Copper

(a) **Copper in Water.**—On the electrolysis at 60° for three hours under an e. m. f. of 4.0 volts of 250 cc. of distilled water containing 0.01 mg. of copper and 1% of sulfuric acid, using the small disk cathode, a dark-colored deposit was obtained. On exposure to the moist fumes of nitric acid the deposit dissolved instantly as shown by the brightening of the electrode. The electrode with adhering droplets of copper nitrate solution was then dipped into a drop of 10% potassium thiocyanate solution acidified with acetic acid, held on a microscope slide, and exposed to pyridine vapors. The characteristic yellowish-green needles of copper pyridine thiocyanate appeared. The dilution in this case amounted to 4 parts of copper in one hundred million.

(b) **Traces of Copper in Nickel Solutions.**—Table IV shows results obtained on electrolysis of nickel nitrate solutions 1% in nitric acid and 2% in sulfuric acid, containing the indicated small quantities of copper. A potential difference of 3.0 volts was applied for four hours at 60–70°. The copper plate obtained was dissolved, redeposited in the small cell and weighed.

TABLE VI

DETERMINATION OF COPPER IN NICKEL SOLUTIONS

| Nickel present, mg. | Copper present, mg. | Copper found, mg. | Error, parts per thousand |
|---|---|---|---|
| 5000.0 | 0.100 | 0.103 | +30 |
| 5000.0 | .200 | .196 | −20 |
| 5000.0 | .500 | .502 | + 4 |
| 5000.0 | 1.000 | 1.008 | + 8 |
| | | Average | ±15 |

Similar results were obtained for traces of copper in zinc solutions.

**Determination of Impurities in Reagent Chemicals.**—Incidental to this work, it was observed that the labels on "C. P." reagent chemicals sold

by prominent manufacturers are often misleading. Table V gives examples, and emphasizes the delicacy of micro-electroanalytical methods.

TABLE V

ANALYSIS OF "PURE" CHEMICALS

| Manufacturer | Chemical | Excerpt from label | Lead found |
|---|---|---|---|
| A | Zinc sulfate | "Heavy Metals, <0.001%" | 0.01% |
| B | Zinc sulfate | "Heavy Metals, 0.000%" | 0.0015% |
| C | Zinc sulfate | (Impurities not indicated but ostensibly negligible) | Trace |
| A | Nickel sulfate | "Tested Purity" | 0.045% |
| C | Nickel nitrate | (Impurities ostensibly negligible) | 0.0005% |

The following are typical examples of the uses of the cell for small volumes.

**Determination of Nickel.**—The solution used contained, in one liter, 40 g. of ammonium sulfate, 340 cc. of ammonia solution and 0.19740 g. of nickel as nickel sulfate; 5-cc. portions were used for the determinations, here as well as in the following examples. The air used for stirring was passed first through concentrated ammonia solution; this not only prevented the loss of ammonia from the electrolyte but maintained in it a practically constant concentration of the dissolved gas. The conditions for the best deposit proved to be rather critical, and were as follows: e. m. f., 2.4–2.5 volts (60–70 milliamperes);[7] time, fifteen to twenty minutes; temperature 60°. Seven such samples were analyzed. The average weight of nickel recovered was 0.988 mg. (0.987 mg., present), the average deviation of the results from this average being ±0.002 mg., with a maximum deviation of 0.004 mg.

**Determination of Tin.**—For this determination ammonium sulfide was found to give more satisfactory results as electrolyte than did oxalic acid. As recommended by A. Fischer,[8] the electrode was first prepared by depositing a thin coat of copper, followed by one of tin from an oxalate solution. The electrolyte consisted of ammonium monosulfide solution containing sodium sulfite (to prevent formation of free sulfur). The best conditions for the electrolysis were found to be: e. m. f., 1.2 volts (1200 milliamperes); time, twenty to thirty minutes; temperature, 60°. After the electrolysis the electrode was washed with water, alcohol, carbon bisulfide, alcohol and ether, in the order given. Several samples, each containing 0.995 mg. of tin, were analyzed. Average weight of tin recovered: 0.996 mg.; average deviation from this average: ±0.003 mg.; maximum deviation, 0.005 mg.

[7] It is not practicable to give current densities, since the area of a fine gauze electrode is not accurately estimable.

[8] Fischer, *Z. anorg. Chem.*, **42**, 382 (1904).

**Determination of Zinc.**—The difficulties met in the macro-determination of zinc are also operative here, and require special attention in working out a satisfactory procedure. From caustic solutions the deposit, while perfectly adherent, tends to assume a bluish-gray, granular form, in which it is subject to some oxidation. Three factors were found to favor this objectionable form: too high a temperature, too low an alkali content, and evolution of hydrogen at the cathode. Electrolytes weakly acid or containing cyanide were entirely unsatisfactory. Experiments showed, however, that by suitably regulating the important variables the caustic medium could be used to give accurate and precise results. The best conditions for the electrolysis, which must be strictly maintained to assure good results, are as follows: temperature, 25°; potassium hydroxide concentration, 10%; e. m. f., 3 volts (150 milliamperes); time, fifteen minutes. Cathodic evolution of hydrogen was prevented by giving the platinum gauze a thin preliminary plate of copper. Since the zinc deposit is very soluble in 10% caustic solution, especial precautions must be taken to wash out all traces of the electrolyte before interrupting the current; errors as great as 5% have been observed from carelessness here. Eleven analyses were made. With 0.898 mg. of zinc present (as C. P. zinc sulfate), the average weight of zinc recovered was 0.899 mg. The average deviation from this average was ±0.003 mg., and the maximum deviation 0.013 mg.

## Summary

1. Two new cells for micro-electroanalysis are described, both suitable for separating extremely small quantities of metallic ions from solutions, but the one designed to electrolyze a few cc., and the other several hundred cc.

2. Descriptions are given for the following determinations employing the cell for large volumes: traces of zinc in aluminum sulfate solutions; traces of lead in zinc sulfate and in nickel nitrate solutions; traces of copper in water and in nickel nitrate solutions; impurities in "chemically pure" reagents. For the small cell the following determinations are described: traces of nickel, of tin and of zinc.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, NORTHWESTERN UNIVERSITY]

# A SIMPLIFIED METHOD OF CALCULATING TANGENTS BY THE THEORY OF LEAST SQUARES[1]

BY FRANK T. GUCKER, JR., AND HERBERT J. BRENNEN

RECEIVED SEPTEMBER 17, 1931 PUBLISHED MARCH 5, 1932

It is frequently necessary to evaluate the tangent to a curve based on experimental measurements. When the data can be represented with sufficient accuracy by a second degree equation $y = c + ax + bx^2$, and the $y$-axis is made to pass through the point at which the tangent is required

$$(dy/dx)_{x=0} = a \qquad (1)$$

Provided the error in the independent variable is negligible in comparison with that in the dependent, $a$ can be determined by the method of *least squares*. The sum of the squares of the deviations of $n$ equally reliable observations becomes a minimum if the partial derivatives of $\Sigma_{n=1}^{n=n}(c + ax + bx^2 - y)^2$ with respect to $a$, $b$ and $c$ are set equal to 0.[2]

Solving the resulting *normal equations* in the convenient determinant form[3] gives

$$a = \begin{vmatrix} n & \Sigma y & \Sigma x^2 \\ \Sigma x & \Sigma xy & \Sigma x^3 \\ \Sigma x^2 & \Sigma x^2 y & \Sigma x^4 \end{vmatrix} \div \begin{vmatrix} n & \Sigma x & \Sigma x^2 \\ \Sigma x & \Sigma x^2 & \Sigma x^3 \\ \Sigma x^2 & \Sigma x^3 & \Sigma x^4 \end{vmatrix} \qquad (2)$$

If now the values of $x$ are taken at *equal intervals on either side*[4] of the $y$-axis, $\Sigma x$ and $\Sigma x^3$ vanish and

$$\left(\frac{dy}{dx}\right)_{x=0} = a = \frac{n\Sigma xy\Sigma x^4 - \Sigma x^2\Sigma x^2\Sigma xy}{n\Sigma x^2\Sigma x^4 - \Sigma x^2\Sigma x^2\Sigma x^2} = \frac{\Sigma xy}{\Sigma x^2} \qquad (3)$$

The restriction to equal intervals does not seriously limit the applicability of the method. Data are usually tabulated at equal intervals and experimental results can easily be obtained thus if subsequent reduction is required.

The simplicity of the method is illustrated in Table I, which gives all the work required to calculate ten values of the coefficient of thermal expansion of sodium chloride solutions from the density at five different temperatures.[5] For convenience, the independent variable is made $x = (t - 25)/5$ and the dependent variable $y = 10^4(D_{10} - Dt)$. Then $y = 0$ when $x = -3$, which further simplifies the summation. By definition

[1] Paper presented before the Buffalo meeting of the American Chemical Society, August 31–September 3, 1931.

[2] *Cf.* Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., 1929, p. 326, for the method applied to the linear equation.

[3] *Ibid.*, p. 584.

[4] Harry M. Roeser, in Scientific Paper No. 388 of the Bureau of Standards, has shown the great advantage of taking observations at equal intervals of the independent variable and gives useful tables for rapid calculation of *all* the coefficients.

[5] "International Critical Tables," Vol. III, p. 79.

$$\alpha = (1/V)(\partial V/\partial T)_P = -(1/D)(\partial D/\partial T)_P \qquad (4)$$

Since $-(dD/dt) = 2 \times 10^{-5}\,(dy/dx)$ and $\Sigma x^2 = 20$, combination with (3) and (4) gives

$$10^4\alpha = \Sigma xy/100D \qquad (5)$$

The whole process of calculating $\alpha$ then consists simply in multiplying each of the three tabulated values of $y$ by the corresponding value of $x$, adding them together and dividing by 100 times the density.

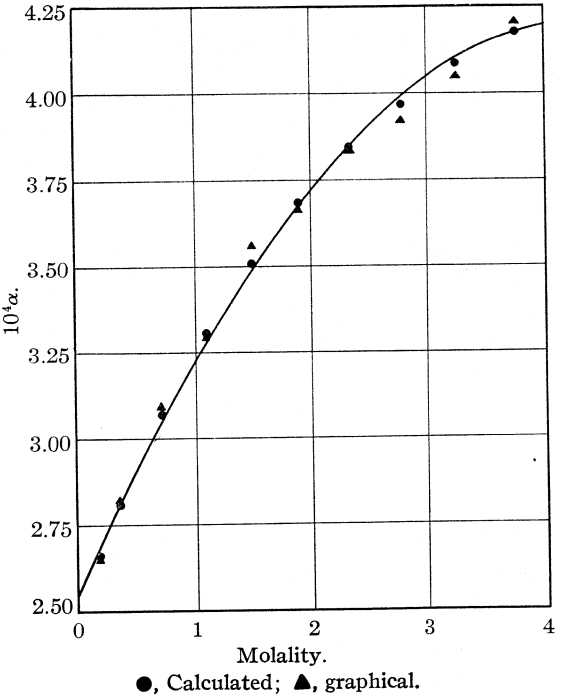


Fig. 1.—Coefficients of expansion of sodium chloride solutions at 25°.

Graphical values of $\alpha$, read off the $D$–$t$ curve by laying a ruler tangent at 25°, are included for comparison. The analytical method is actually more rapid than the graphical. It is also free from the personal bias of judging tangents and gives more concordant results. The average deviations of the graphical values of $\alpha$ from the curve are nearly three times those of the calculated values. This is shown by Fig. 1, where the values of $\alpha$ for sodium chloride solutions at 25° are plotted against concentration. The difference might be greater still if the density data in the tables had not already been smoothed so that the graphical curves can be fitted exactly to the points.

TABLE I

DATA AND CALCULATED VALUES

| Wt. % of NaCl | $t$.. 10 / $x$..−3 | 20 / −1 | 30 / 1 | 40 / 3 | $\Sigma xy$ | $d_{25}$ | $\alpha \times 10^4$ Calcd. | $\alpha \times 10^4$ Graph. |
|---|---|---|---|---|---|---|---|---|
| | $y$ | | | | | | | |
| 1 | 0.0 | 17.3 | 44.6 | 79.9 | 267.0 | 1.0041 | 2.659 | 2.64 |
| 2 | .0 | 19.6 | 48.5 | 84.9 | 283.6 | 1.0111 | 2.805 | 2.82 |
| 4 | .0 | 24.0 | 55.9 | 94.3 | 314.8 | 1.0253 | 3.070 | 3.09 |
| 6 | .0 | 28.1 | 62.7 | 103.0 | 343.6 | 1.0396 | 3.305 | 3.34 |
| 8 | .0 | 31.8 | 68.8 | 110.9 | 369.7 | 1.0541 | 3.507 | 3.56 |
| 10 | .0 | 35.1 | 74.3 | 118.1 | 393.5 | 1.0688 | 3.682 | 3.66 |
| 12 | .0 | 38.0 | 79.3 | 124.7 | 415.4 | 1.0837 | 3.833 | 3.83 |
| 14 | .0 | 40.6 | 84.0 | 130.9 | 436.1 | 1.0987 | 3.969 | 3.92 |
| 16 | .0 | 43.5 | 88.5 | 136.8 | 455.4 | 1.1140 | 4.088 | 4.05 |
| 18 | .0 | 45.3 | 92.8 | 142.5 | 475.0 | 1.1295 | 4.205 | 4.18 |
| | | | | | Average deviation from curve | | ±0.018 | ±0.05 |

## Summary

In conclusion, a simplified method of calculating tangents from the theory of least squares has been presented. By choosing equally spaced positive and negative values of the independent variable and making the $y$-axis pass through the point at which the tangent is desired, $dy/dx = \Sigma xy/\Sigma x^2$. Tangents may thus be calculated more rapidly and precisely than by graphical means. The method may be applied in many other cases beside that used as an illustration.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# THE COLLISION AREAS AND SHAPES OF CARBON CHAIN MOLECULES IN THE GASEOUS STATE: NORMAL-HEPTANE, NORMAL-OCTANE, NORMAL-NONANE

BY RALPH M. MELAVEN AND EDWARD MACK, JR.

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In a chapter on "The Effects of Molecular Dissymmetry on Properties of Matter," Langmuir presents[1] plausible reasons, based on surface energy considerations, for believing that a molecule such as palmitic acid, when isolated in the gas phase or in solution, has its carbon chain coiled up into an approximately spherical form rather than fully extended as a straight chain. Du Noüy concludes that the chain of the giant protein molecules is, in certain situations, folded up[2] into a parallelepiped or prism-like form, and Hauser[3] recently interprets the x-ray diffraction patterns, obtained when rubber is stretched and unstretched, as meaning that the

[1] Alexander, "Colloid Chemistry," The Chemical Catalog Co., New York, 1926, Vol. I, pp. 525–546.

[2] Du Noüy, *J. Biol. Chem.*, **64**, 595 (1925).

[3] Hauser, *Ind. Eng. Chem.*, **21**, 249 (1929).

rubber molecule is coiled up in a helix before stretching and becomes pulled out during the stretching process. Indeed these views all bear a resemblance to Frankland's suggestion many years ago that a carbon chain may be coiled into a helix—a suggestion borne out by the work of Pickard and Kenyon on the dependence of rotatory power on chemical constitution.[4] The present investigation was undertaken to determine whether the molecules of normal heptane, octane and nonane, in the gas phase, are extended or coiled up or what their shapes are.

The method employed involves a calculation of the collision area of the molecule from gaseous viscosity measurements, and then, in an attempt to obtain a definite idea of the average molecular shape, a comparison of the numerical value of this collision area with the numerical value of the average cross-sectional area of a *model of the molecule made to scale.* For the purpose of estimating such model areas a shadow-graphic scheme was suggested and applied in a previous paper.[5] That scheme, with some modification, serves satisfactorily in the present investigation. In the meantime, also, the data regarding the sizes of atomic domains, and the distances between atomic centers, and the general background of information needed to construct good models, have been greatly improved.

The details of the model area technique will be given later in this paper after the experimental procedure and the gaseous viscosity data have been presented.

## Experimental Procedure

We have made use of the form of apparatus set up by Lowry and Nasini,[6] which in turn closely resembles that employed by Rankine and Smith.[7] Figure 1 shows the arrangements. The glass parts were all made of Pyrex glass. The vapor of the volatile liquid (which itself was stored in the reservoir tube $R_1$) was allowed to transpire through the capillary tube C from a region of higher temperature $T_1$ to a region of lower temperature $T_2$, and the viscosity was calculated in the usual way from the time of transpiration, the dimensions of the capillary, and the pressure head of the transpiring vapor.

The liquid, *e. g.*, heptane, was boiled out to remove dissolved gases, and then in a small sealed tube, A, which was completely filled with the liquid to avoid the presence of air, was introduced into the apparatus in the chamber B. The whole system was thoroughly exhausted through a connection at P with a mercury vapor diffusion pump, and sealed at P. The tube A was then broken by allowing the slug of iron I, encased in glass and magnetically controlled, to fall. The liquid was distilled into the reservoir $R_1$, which was cooled by pouring some ether over it. During the process of breaking the glass container A and the subsequent distillation of the liquid into $R_1$, the glass trap D prevented the entrance of small pieces of broken glass into the capillary. The system was sealed off at $S_1$ and $S_2$, and the accessory loading tubes (drawn in the figure with dotted lines) removed.

[4] Pickard and Kenyon, *J. Chem. Soc.*, **103**, 1923 (1913).

[5] Mack, THIS JOURNAL, **47**, 2468 (1925).

[6] Lowry and Nasini, *Proc. Roy. Soc.* (London), **A123**, 686 (1929); Nasini, 692, 704.

[7] Rankine, *ibid.*, **A88**, 575 (1913); Smith, *ibid.*, **A106**, 83 (1924).

During a run the water thermostat $T_1$ was automatically controlled at a convenient temperature, within 0.01°, and the temperature of $T_2$ was maintained at 0° with crushed ice. The rate at which transpiration occurred was followed by measuring the rate of travel of the liquid meniscus down the small tube $R_1$. This tube was carefully calibrated and was mounted over a milk-white porcelain scale. The position of the meniscus was observed through the glass front of the thermostat, with a reading microscope, and interpolations between scale divisions made with a filar micrometer. From the volume of the escaped liquid, and its density, the mass transpired in a given time was calculated. The densities of heptane, octane and nonane at the thermostat temperatures were calculated from the following general empirical formula, where $t_s$ is 0°, $t$ is the temperature at which the density is sought and $d_s$ is the density at 0°.

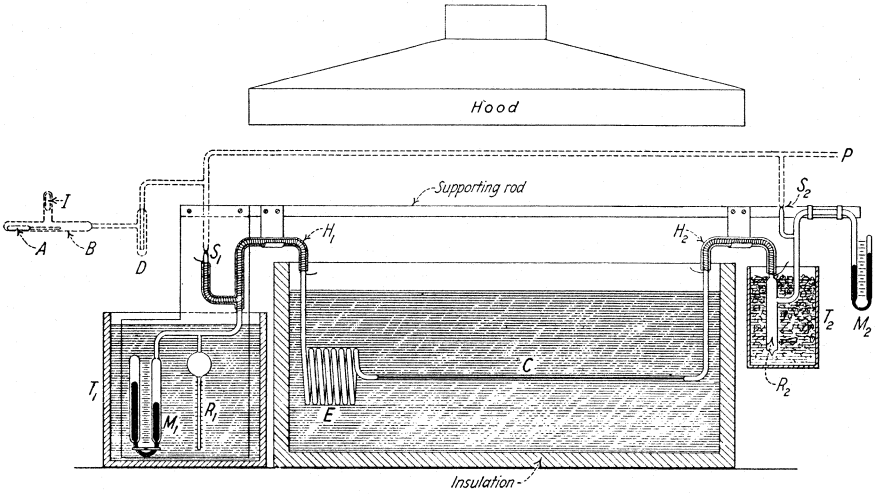


Fig. 1.

$$\text{Density}^8 = [d_s + 10^{-3}\alpha(t - t_s) + 10^{-6}\beta(t - t_s) + 10^{-9}\gamma(t - t_s)^3] \pm 10^{-4}\Delta$$

For *n*-heptane: $d_s = 0.70048$; $\alpha = -0.8476$; $\beta = 0.1880$; $\gamma = -5.23$
For *n*-octane: $d_s = 0.71848$; $\alpha = -0.8239$; $\beta = 0.4459$; $\gamma = -5.293$
For *n*-nonane: $d_s = 0.7333$; $\alpha = -0.75$; $\beta = -0.455$

The two portions, $H_1$ and $H_2$, of the system which project above the temperature-controlled baths were heated electrically to prevent condensation of the vapor in them. The capillary tube C was supported in a large thermostatically controlled (±0.5°) and well-stirred tank of tempering oil, with arrangements for heating the oil electrically to temperatures of 100, 150, 200 and 250°. The fumes from the hot oil were carried away by the hood which hung over the apparatus. The glass coil E gave the transpiring vapor a chance to attain the temperature of the oil-bath before reaching the capillary. The driving pressure and the condensing pressure were both observed with reading microscopes on the scales of the mercury manometers $M_1$ and $M_2$, respectively. In general the driving pressure was somewhat lower and the condensing pressure somewhat higher than the true vapor pressures.

The capillary C was selected from a stock of small Pyrex capillary tubes. The

[8] "International Critical Tables," The McGraw-Hill Book Co., Inc., New York, 1929, Vol. III, pp. 29–30.

uniformity of bore was carefully tested at 5-cm. intervals by measuring the length of a mercury thread with a comparator, and then a section of very uniform bore was cut out of the much longer piece for use. The capillary, when sealed into the apparatus, had a length of 52.2 cm. measured on a standard brass scale, and an average radius of 0.01449 cm.

After a transpiration, the liquid which collected in the condenser $R_2$ could, of course, be returned to $R_1$ by reverse distillation, for further runs.

With this apparatus we were able to obtain most satisfactorily reproducible results. We checked Lowry and Nasini's[6] viscosity results for toluene very closely. Ordinarily it was possible to check transpiration times over a period of two to three hours to within ten or twelve seconds and, in the case of nonane, two transpirations of 105 minutes each checked within two seconds.

The exceptionally pure samples of *n*-heptane, *n*-octane and *n*-nonane, with corrected boiling points, respectively of 98.38, 125.59, and 150.71°, were very kindly supplied to us by Mr. Thomas Midgley, Jr.

**Viscosity Data.**—The viscosity, $\eta$, of the vapor was calculated from the experimental data by means of the equation,

$$\eta = \frac{\pi r^4 (p_1^2 - p_2^2)t}{16\, l\, p_0\, m} \cdot \frac{T_0}{T_1} \cdot d$$

where $r$ and $l$ are the radius and length of the capillary, $p_1$ and $p_2$ the driving and condensing pressures, $p_0$ is normal pressure (76 cm.), $m$ is the mass transpired in time $t$, $T_0$ is 273° absolute and $T_1$ the absolute temperature of the capillary, and $d$ is the density of the vapor at N. T. P.

Corrections for expansion of the Pyrex capillary tube with rising temperature are small enough to be neglected, as are also the kinetic energy corrections. The correction for slip, however, is appreciable and was made. This was done with the equation

$$\eta \text{ (corrected)} = \eta\,(1 + 4\,\zeta/r)$$

where $r$ is the radius of the capillary, and $\zeta$, the coefficient of slip, is given by the equation

$$\zeta = 1.70\,\eta\,\sqrt{3RT/M}/(p_1 + p_2)$$

Reynolds' criterion was applied to determine whether the experimental conditions of transpiration had been correctly chosen to insure viscous flow and not to allow turbulent flow. This criterion, expressed in the form

$$rdv/\eta < 1000$$

demands that the left-hand side be less than about 1000. Here $r$ is the radius (in cm.) of the capillary, $d$ is the density (in g./cc.) of the vapor, $v$ is the velocity of efflux of vapor (cc./sec./sq. cm. of capillary cross section) and $\eta$ is the viscosity (g./cm./sec.). In all of the measurements reported here, this term is considerably less than 1000. For example, in the case of heptane at 100°, the most rapid transpiration, it has a value of about 29.

In Table I are listed the viscosity data, including the viscosities corrected for slip (in the last column).

TABLE I

VISCOSITY DATA FOR HEPTANE, OCTANE AND NONANE

| | Temp. (°C.) of capillary | $p_1$, cm. | $p_2$, cm. | Rate of transpiration, g./hr. | $\eta \times 10^{-4}$ | $\eta$ (corrected) $\times 10^{-4}$ |
|---|---|---|---|---|---|---|
| *n*-Heptane | 100.4[a] | 6.33 | 2.10 | 0.1721 | 0.711 | 0.717 |
| | 150.5 | 6.39 | 2.18 | .1356 | .803 | .811 |
| | 202.2 | 6.52 | 2.18 | .1115 | .910 | .922 |
| | 251.6 | 6.60 | 2.34 | .09331 | .994 | 1.08 |
| *n*-Octane | 100.4 | 3.04 | 0.800 | .05054 | .664 | 0.675 |
| | 150.6 | 3.04 | .800 | .03996 | .740 | .750 |
| | 202.2 | 3.035 | .830 | .03154 | .828 | .848 |
| | 250.9 | 3.05 | .845 | .02645 | .903 | .928 |
| *n*-Nonane | 100.3 | 2.29 | .401 | .03593 | .620 | .633 |
| | 150.3 | 2.29 | .478 | .02830 | .685 | .702 |
| | 202.1 | 2.29 | .500 | .02271 | .760 | .781 |
| | 250.8 | 2.282 | .555 | .01858 | .824 | .851 |

[a] Temperatures were read on thermometers, corrected for stem emergence, and standardized against Bureau of Standards thermometers.

**Sutherland Constants.**—The Sutherland equation

$$\eta = \frac{k \cdot T^{3/2}}{C + T}$$

was employed to obtain the Sutherland constant $C$. The different values of $T^{3/2}/\eta$ at the different temperatures, $T$, were plotted against $T$, and the straight line was extrapolated to obtain the negative intercept on the temperature axis. The values of these intercepts, which are the Sutherland constants, were as follows: *n*-heptane, $C = 445$; *n*-octane, $C = 337$; *n*-nonane, $C = 276$.

The Sutherland constants, obtained in this way, are necessarily approximate values only, because of the very considerable extrapolation involved. They represent, however, the best obtainable values under present circumstances and, in view of the fact that the data points lie almost exactly on a straight line, the Sutherland constants are probably not very much different from the true values.

In this connection, an empirical equation, $C = 1.47\ T_b$, has been suggested,[9] to predict the Sutherland constant from the boiling point on the absolute scale. Titani,[10] who has carried out a large number of measurements of the viscosities of organic vapors, compares his results for the Sutherland constants of ethane, propane, butane and a number of other substances, with the values predicted empirically from the boiling points. The agreement is not particularly good. Arnold[11] uses the Vogel equa-

[9] Vogel, *Ann. Physik*, **43**, 1235 (1914).

[10] Titani, *Bull. Chem. Soc. Japan*, **4**, 277 (1929); **5**, 98 (1930).

[11] Arnold, *Ind. Eng. Chem.*, **22**, 1091 (1930).

tion to obtain Sutherland constants, and then by a further treatment of these, calculates diffusion coefficients.

While this empirical relationship may serve a useful purpose in arriving at rough estimates of Sutherland constants for certain kinds of molecules, particularly small molecules, it can hardly be universally valid. One would expect it to break down entirely in the case of even moderately large and complicated molecules. During the boiling process, the forces which come into play to prevent the escape of a molecule from the liquid are active, undoubtedly, over practically the whole surface of the molecule, or at least over a large fraction of the surface. In the encounter of two *gaseous* molecules, if the molecules are small, it is possible that a large part of the van der Waals field of force of each molecule becomes involved in the act of attraction, when the two molecules approach closely. But, on the other hand, as the molecules become larger and increasingly complicated, so that the spacial arrangement of atoms and groups of atoms interferes appreciably with close approach of the effective centers of the two molecules, in increasing measure will smaller and smaller portions of the whole molecular surface be involved in the collision. Since the Sutherland constant is a measure of the attractive force during collision, it is therefore to be expected that the Sutherland constants may decrease, through a series of larger and larger molecules, while at the same time the boiling points are increasing.

Thus the present values for Sutherland constants for *n*-heptane, *n*-octane and *n*-nonane have just been given as 445, 337, 276, respectively; the values calculated from the boiling points by Vogel's equation are 546, 586, 613. The empirically calculated values for benzene and toluene are 372 and 564, whereas Lowry and Nasini[6] report experimental values of 380 and 370; and we would predict that the Sutherland constants for ethyl-, propyl-, butylbenzene, etc., will be found to be successively smaller, in spite of the increasing boiling points.

**Collision Areas.**—The collision areas of the heptane, octane and nonane molecules were calculated with Chapman's[12] equation

$$\overline{A} = \frac{0.0868\,(1 + \epsilon_\alpha)\, d_0 \overline{V}}{n\eta\,[1 + (C/T)]}$$

where $\overline{A}$ is the collision area of the molecule considered as an attracting, elastic sphere; $d_0$ is the density of the vapor at standard conditions; $\overline{V}$ is the average velocity of the molecules at temperature $T$; $n$ is the number of molecules per cc. at standard conditions; $\eta$ is the viscosity of the vapor at temperature $T$; $C$ is Sutherland's constant; $(1 + \epsilon_\alpha)$ is a correcting term, but in the present cases differs from unity by less than 1%, and hence is not applied.

[12] Chapman, *Trans. Roy. Soc. London*, **A216**, 347 (1916).

The results of the calculation of the collision areas, expressed in square Ångström units, are: *n*-heptane, 26.7; *n*-octane, 34.9; *n*-nonane, 42.5. Rankine and Smith have obtained the value 7.72 for methane;[13] and Titani[10] gives the values 10.63, for ethane, 13.5 for propane, 16.1 for *n*-butane, and 17.0 for isobutane. These collision areas, calculated from the Chapman equation, are independent of temperature, and may be false to the extent to which the Sutherland model does not hold; and may be in error because the Chapman equation is strictly applicable only to spherical molecules, such for example as the rare gas atoms. It has not yet been possible to develop an equation for an assembly of molecules with other than spherical symmetry. It does seem likely, however, that non-spherical molecules, if approaching one another with an equal degree of probability from all directions, and if oriented with respect to one another in a purely chance fashion, would behave on the average effectively as spheres. At any rate the collision areas just listed are of the proper order of magnitude and are very self-consistent.

**Method for Obtaining Model Areas.**—In a paper,[14] soon to be published, where the hydrogen atom size is discussed, it is pointed out that the average methane molecule, although of tetrahedral structure, is probably spinning rapidly enough to present itself as a sphere of revolution in molecular encounters in the gaseous state. We can, therefore, calculate its *effective radius* from Rankine and Smith's value of 7.72 sq. Å. for the average cross-sectional area. The result is 1.57 Å. Further, since the distance between the carbon nucleus and the nucleus of a hydrogen atom bonded chemically to the carbon as in methane, is calculated[14] to be about 1.08 Å., the atomic domain, or electron bulge beyond the hydrogen nucleus, under the conditions of gaseous molecule bombardment, is therefore 0.49 Å., or about 0.50 Å. With these dimensions in mind, and with the assumption of tetrahedral carbon bonds, we may proceed to build models of the longer carbon chain molecules. These models, of course, represent the sizes of molecules in collision. Between collisions the atomic domains of the hydrogen atoms around the outer surface of the molecules may enlarge considerably. But the impact of encounter may be thought of as virtually compressing these domains, and the outer surface envelope of the model corresponds to the surface of a molecule when battered in by collision.

Figure 2 (a) gives the model of ethane with an end view at (b). The distance between the nuclei of the two carbon atoms is taken as 1.54 Å. That the methyl groups would be spinning about the $x$–$x$ axis rapidly enough to make the ethane molecule effectively a cylinder of revolution can be shown by the same reasoning employed in the case of methane.[14]

[13] Rankine and Smith, *Phil. Mag.*, **42**, 615 (1921).

[14] Mack, THIS JOURNAL, "The Spacing of Non-polar Molecules in Crystal Lattices."

The molecule would also be spinning end over end about the $y$–$y$ axis and the $z$–$z$ axis (the latter perpendicular to the plane of the paper in (a)). Such end over end spins are to be expected from the partition of energy among the different active degrees of freedom as indicated by the value of the ratio of specific heats, 1.21. However, because of the relatively considerably smaller frequencies of the end over end rotations, the ethane molecule would probably present itself in molecular encounters only partially as a sphere and much more nearly only as a cylinder of revolution, with a length of about 3.25 Å., and a radius of about 1.52 Å., and with the end edges rounded off to the hydrogen atom domain curvature, as shown in Fig. 2 (a). At least, the molecule may now be treated as a cylinder, rather than as a sphere, for the purpose of illustrating the shadow-graphic method of estimating the average cross-sectional area.

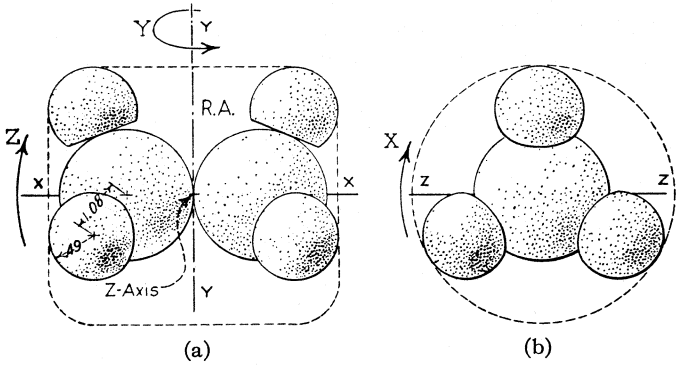


Fig. 2.

Such a cylindrical molecule of ethane would, in the gaseous state, be continuously bumped by neighboring molecules which drive in upon it from all directions. All directions of approach may be supposed to be equally probable. The target area which the molecule presents to this bombardment would therefore be the average of all its cross-sectional areas viewed from all directions. Similarly, every molecule which approaches will have the opportunity, because of its chaotic spin, of orientation in any possible position, at the instant of impact; or at least this will be true if there are no forces acting to swing the axes of the two colliding molecules into certain definite positions with respect to one another (Keesom orientation). On the assumption that there are no orientating forces of this sort the target area of a bombarding molecule would also be its average cross-sectional area viewed from all directions.

The counterpart of this with the model would be the average of all the cross-sectional areas of the model when viewed from all positions. Conceivably such an average could be obtained by integration of the cross-

sectional area of the model turned through the proper angles. But such an integration for most of the ordinary molecules would, as Rankine[15] has pointed out, be exceedingly difficult and laborious. Another method, very simple and satisfactory enough for the purpose in view, is the shadow-graphic method, already mentioned. A model is made to scale (one inch for an Ångström unit is found to give a very convenient model size), and mounted on a support provided with two protractor circles and arranged so that the model can be brought into any orientation by dipping and turning motions. The cross-sectional area of the model in any particular position is obtained by throwing a shadow of it, with parallel light, onto a paper screen, and measuring the area of the shadow in square inches with a planimeter.

Naturally it would be impossible to take enough shadow areas to correspond with all of the infinitely large number of positions around the model from which it could be viewed. Fortunately, only a few positions are necessary, about a dozen equally spaced as to angle, around the model. It can be shown that as the number of positions increases, the average shadow area very rapidly approaches an asymptotic value.

For example, let us take the case of ethane. Imagine that the model of Fig. 2 (a) is placed in a polar axis of a regular octahedron. If we view the model along the axes of the octahedron, *i. e.*, from positions 90° apart, there are six cross-sectional areas, namely, those viewed from above, from below, from right, from left, from in front and from behind. Pairs of shadows taken from opposite ends of polar axes are exactly alike; and we need take only three shadows, therefore, to obtain the average cross-sectional area with respect to approach positions 90° apart. These three shadow areas are 9.5, 9.5 and 7.4 sq. inches; the average is 8.8.

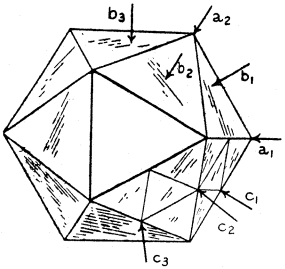

Fig. 3.

Now let us place the ethane model in one of the axes, $a_1$ (Fig. 3), of an icosahedron, the polyhedron having the largest number of regular faces that can be inscribed in a sphere. We may now view the model from the twelve summits of the icosahedron, from positions 63°26′ apart; and here again the two areas obtained from opposite ends of the same polar axis are of course identical. We need, therefore, to take six shadows, one along the line $a_1$ and five along the lines $a_2$, as shown in Fig. 3. All of the $a_2$ shadows are identical for a cylindrical model such as ethane. The average of these six shadows is 10.0 sq. inches.

Again, let us view the model from the twenty positions, 41°50′ apart,

[15] Rankine, *Trans. Faraday Soc.*, **17**, Part 3, 1 (1922); *Proc. Phys. Soc.* (*London*), **33**, Part 5, 362 (1921).

corresponding to the centers of the twenty flat equilateral triangular faces of the icosahedron, namely, along $b_1$, $b_2$ and $b_3$, etc., of Fig. 3, with the long axis of the ethane cylinder placed along $b_2$. The average of the ten required shadows is 10.1 sq. inches.

Finally, if the equilateral triangle faces of the icosahedron are all divided up into four smaller triangles, with an edge length equal to one-half the original edge, and the model is viewed from all of the thirty edge-midpoints, as well as from the twelve summits of the icosahedron, we view the model from forty-two positions which are almost, although not exactly equally spaced as to angle. The north pole distances (N. P. D.) and longitudes of the positions from which the twenty-one required shadows are taken are as follows: one shadow from the north pole, along the line $a_1$; five shadows from points $c_1$, N. P. D., 31°45′, long. 0, 72, 144, 216 and 288°; five shadows from points $c_2$, N. P. D., 58°17′, long. 36, 108, 180, 252 and 324°; five shadows from points $a_2$, N. P. D., 63°26′, long. 0, 72, 144, 216 and 288°; five shadows from points $c_3$, N. P. D. 90°, long. 18, 90, 162, 234 and 306°.[16] The average of the twenty-one shadows is 10.1 sq. inches.

It is evident from a cylinder such as the ethane model that the average cross-sectional area very rapidly approaches an asymptotic value, and that for most purposes the average shadow taken from six positions, *i. e.*, from the poles of an icosahedron, would be sufficiently close to the asymptotic value. Later, in connection with octane it will be shown that even with a much more elongated cylinder, departing much more than ethane does from spherical form, the six-shadow average is satisfactory.

From this model of the ethane molecule, and from the shadow-graphic estimation of its average cross-sectional area, a collision area of 10.1 sq. Å. is predicted for the gaseous ethane molecule. It is further to be noted that in measuring the area of the shadows of the ethane molecule, and also of the other models in general, the reëntrant angle as shown at R. A. in Fig. 2 (a) is neglected; that is, the surface envelope of the model is drawn straight across from hydrogen atom to hydrogen atom. The justification of this procedure is two-fold; in the first place, the space included in such a reëntrant angle is far too narrow to permit the passage or entrance of a bombarding molecule, or even any appreciable portion of it; in the second place, the size of the hydrogen atom domain is really a great deal larger than that shown in Fig. 2. It is pounded down to the given size by molecular impact, and it seems reasonable to suppose that in such elastic encounters the atomic domain of the hydrogen, fluid-like, is flattened out and is squeezed into neighboring crevices corresponding to reëntrant angles.

[16] For a list of these angular positions see "The Collected Mathematical Papers" of Arthur Cayley, Cambridge University Press, 1896, Vol. X, pp. 270–273.

If, on the other hand, the end over end rotations of the ethane molecule were rapid enough to cause the molecule to behave effectively as a sphere of revolution in molecular encounters, we would expect a collision area of 12.6 sq. Å., taking as a radius the distance from the center of the molecule out to the periphery of a hydrogen atom of domain radius 0.50 Å. The fact that Titani's experimental value for ethane, 10.6 sq. Å., lies between the area values predicted from the two shapes, 10.1 from the cylinder and 12.6 from the sphere, but resembles much more nearly that of the cylinder, justifies the expectation that the molecule will behave effectively as a cylinder, and only partially and to a very limited degree as a sphere. This expectation also finds support in an argument based on the probable frequencies of the end over end spins of the ethane molecule, as may be shown from the following considerations.

From the equi-partition principle it follows that $E$, the energy of spin of the ethane molecule, *e. g.*, about the $z$–$z$ axis of Fig. 2, is given by the equation, $E = {}^1/_2\, kT$, where $k$ is the Boltzmann constant and $T$ the absolute temperature. At 25°, $E$ equals about $2.04 \times 10^{-14}$ ergs. The frequency of spin, $\nu$, may then be calculated from the relationship, $\nu = \sqrt{2E/I}/2\pi$, where $I$, the moment of inertia of rotation about the $z$–$z$ axis, can readily be shown to be about $36.2 \times 10^{-40}$. The calculated frequency is about $53.3 \times 10^{10}$ rotations per second, which means that the time for one complete rotation is about $18.7 \times 10^{-13}$ seconds, and for rotation through, let us say 120°, about $6.2 \times 10^{-13}$ seconds. Since both molecules which partake in the collision are spinning, we may cut this time to $3.1 \times 10^{-13}$ seconds. But during this time interval, the approaching molecule will travel, on the average, a distance of a little more than 1.5 Å., as calculated from the equation $u = \sqrt{3kT/m}$. Even keeping in mind the fact that there is a simultaneous spin about the $y$–$y$ axis (as well as the $z$–$z$ axis which is here being considered), it yet seems very likely that the approaching molecule will be able to penetrate deeply into the spherical envelope in regions where the hydrogen atoms do not happen to be at the instant of impact. Thus we reach the probable conclusion that the end over end spins are relatively so slow that they fail to guard the spherical envelope against invasion, and hence the molecule falls short by a considerable margin of being able to present itself as a sphere of revolution.

**Propane, Butane and Isobutane.**—The cross-sectional areas of the models of propane, butane and isobutane are obtained by the same sort of treatment as that just described for ethane.

In propane, with its carbon atoms assumed to be linked together at tetrahedral angles, $C\!\diagup\!\overset{C}{\diagdown}\!C$, the frequencies of spin about the long axis of the molecule and of the end over end spins, are considerably too small to make the molecule effective either as a cylinder or as a sphere of revo-

lution, although the two end methyl groups are undoubtedly spinning rapidly enough about the bond which connects them to the middle carbon atom to present themselves as rings of revolution. The average shadow area (twelve positions) for such a propane model, with hydrogen atoms of domain radius 0.50 and with the methyl groups in the form of rings, is 13.0 sq. inches.

Similarly, butane, C  C, gives an average shadow area of 14.5 sq. inches. Isobutane, with three spinning methyl groups connected to the fourth carbon, averages 17.0 sq. inches.

These shadow areas, together with Titani's collision area results (Titani gives them as diameters) are collected in Table II. In the last column, for the sake of comparison, the cross-sectional areas of the very improbable spheres of revolutions are given.

TABLE II

COMPARISON OF COLLISION AREAS WITH MODEL AREAS

| | | Collision area, sq. Å. | Average shadow area of model, sq. inches* | Average cross-sectional area of sphere of revolution |
|---|---|---|---|---|
| Methane | $CH_4$ | 7.72 | 7.72 | 7.72 |
| Ethane | $C_2H_6$ | 10.63 | 10.1 | 12.6 |
| Propane | $C_3H_8$ | 13.53 | 13.0 | 22.7 |
| Butane | $C_4H_{10}$ | 16.11 | 14.5 | 27.7 |
| Isobutane | $C_4H_{10}$ | 17.05 | 17.0 | 22.4 |

In the case of methane, the size of the hydrogen atom domain is, of course, chosen to make the model cross-sectional area agree exactly with Rankine and Smith's collision area, 7.72 sq. Å. The divergencies between the other collision area values and the corresponding shadow values are in part attributable to the fact that the hydrogen atom domain probably increases slightly with the ascent of the homologous series, as will be explained later (and no account has been taken of this effect in the shadow areas presented in Table II); and also in part to the fact, already mentioned in the case of propane, that no allowance whatever has been made for the effect of the spins, except for the end methyl groups, and undoubtedly the effect would be to enlarge the shadow areas in some measure.

Inspection of the table shows, however, in spite of our neglect of these second order effects, that agreement between the two columns for ethane, propane, butane and isobutane is quite good; sufficiently good, in fact, to make this whole scheme of model construction and shadow-graphic treatment of the average area a very plausible procedure. On the basis of this foundation of justification, we may now proceed to a consideration of the probable shapes of the molecules of longer carbon atom chains.

***n*-Heptane, *n*-Octane, *n*-Nonane.**—In the discussion of the molecules of heptane, octane and nonane, only octane will be considered in detail,

in the interests of brevity, since the other two are treated in precisely the same manner. The results for all three are listed below in Table III.

If a normal octane molecule in the gaseous state exists in the most extended possible form, it would have the shape shown in Fig. 4, with all the carbon valencies at tetrahedral angles. The frequency of spin of such a molecule about its long axis would be rapid enough compared with the relatively slow translatory motion of a heavy approaching molecule, to present the bombarded molecule as a cylinder of revolution. The end over end spins would be much too slow to prevent invasion; in fact deep penetration into the spherical envelope would be expected. It is justifiable, then, to treat such a hypothetical gaseous molecule as being effectively a cylinder and to proceed to an estimation of its average cross-sectional area by the shadow-graphic method.

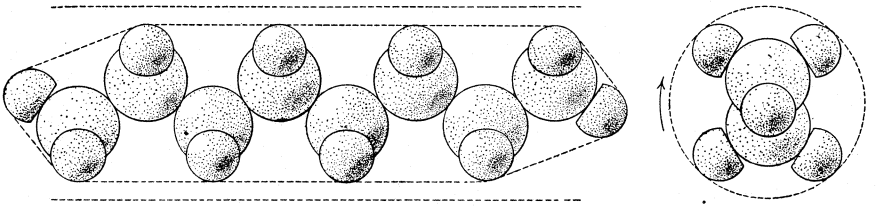

Fig. 4.

Before this can be done, however, there is another very important matter to be taken into consideration. In the case of the collision of two methane molecules it is probably true that not more than one hydrogen atom on each molecule is on the average involved in the impact, or takes part in the act of repulsion which ultimately forces the two molecules apart, and which also determines the depth to which the molecular surface envelopes are compressed. But as we go up the series from ethane to nonane, finding an increasing number of hydrogen atoms per molecule and in general a decreasing velocity of molecular spin, we would expect a larger and larger number of hydrogen atoms to be involved in the impact. Judging from the manner in which hydrogen atoms are studded over the surface of an octane molecule, we might expect about four atoms, on the average, to partake in the collision. Since the average force of impact for all of these molecules, in spite of their different masses, is the same (at the same temperature), naturally the extent to which the hydrogen atom domain is battered in will not be as great where several atoms receive the impact as it will where one atom unaided bears the brunt of the same blow. Or to put the matter possibly more correctly, a set of several dipoles (hydrogen atoms) driven against another set of several will not approach as closely as one dipole driven with the same force against a single dipole.

If we assume that the repulsion between two such approaching hydrogen atoms is developed entirely by the two nuclei, $+ \ldots\ldots +$, the repulsive force would be inversely proportional to $s^2$, where $s$ is the distance between the two positive changes. If, on the other hand, we assume that the repulsive force is due to the mutual interaction of two dipoles, $+-\ldots\ldots-+$, with the full electronic charge active, none of it shielded out, the force would be inversely proportional to $s^4$. Actually the situation is probably somewhere between these two, since undoubtedly part of the electron density in the hydrogen atom domain is to be found surrounding the positive nucleus on all sides. Perhaps the best approximation that can be made here is to assume a third power law of repulsion. If this is done $s$, the distance of closest approach of the two hydrogen nuclei, would be about $2 \times 0.49$ Å. $\times \sqrt[3]{4}$, when four hydrogen atoms on each colliding molecule take part in the act of impact. This distance is 1.55 Å., and means that the radius of the hydrogen atom domain in octane would be about 0.78 Å., as compared to 0.49 Å. in methane. With a fourth power law the domain radius[17] would be about 0.70 Å. The effective size of the hydrogen atom domain undoubtedly increases somewhat regularly in the ascent of the homologous series. For this reason, the model areas in the previously given Table II are all, with the exception of methane, a little too small.

Let us return now to the shadow area of the octane model (most extended and with hydrogen domain radius of 0.78). The average shadows at the various numbers of equal angle positions from which a model can be viewed are given here again to prove how rapidly the asymptotic average is approached even for such an extended form as this octane cylinder.

| Number of positions | 6 | 12 | 20 | 42 |
|---|---|---|---|---|
| Average shadow area (sq. inches) | 38.7 | 39.95 | 39.9 | 39.95 |

Thus the extended octane model yields a shadow area of about 40.0. This is too large to represent the octane molecule. The calculated collision area of the molecule from the viscosity data is 34.9 sq. Å. The actual molecule is therefore not extended, but exists in a smaller, more collapsed form.

The most highly compact helix into which the octane model chain can be wound, by rotating the carbon atoms on the bonds which connect them, but without changing the tetrahedral angles, is practically a sphere, shown in Fig. 5, and gives an average shadow area (when the outside surface of

[17] The authors recognize that this estimation of the hydrogen domain size is quite inadequate. Eventually, no doubt, a precise calculation can be made when the wave function in the system C–H is known. At any rate the change in the domain size dependent on the number of hydrogens partaking in the impact is too small relative to the over-all dimensions of the molecules to affect the nature of the general conclusions to be drawn.

the molecule is again studded over with hydrogen atoms with a domain radius of 0.78 Å.) of 26.4 sq. inches. This is too small. Clearly, the actual octane molecule possesses a shape somewhere between that of the most extended chain and the most compact helix. It is probably a loosely wound helix.

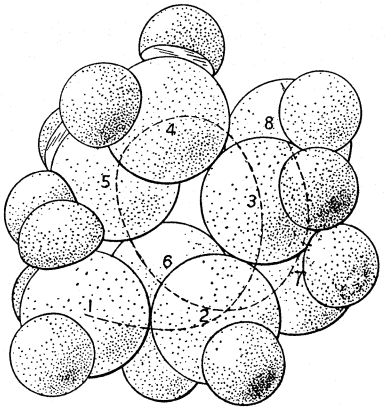

Fig. 5.

The tightness with which the helical chain can be packed together seems to be determined by the presence of hydrogen atoms of about the size found in organic liquids.[14] Such atoms along the interior portions of the helix would not be subject to direct bombardment, would not be compressed as much as the hydrogen atoms on the surface and would prevent the formation of anything tighter than a very loose spiral. It is somewhat difficult to represent this form in a drawing, but in Fig. 6 an attempt is made to show how the large-sized hydrogen atoms condition the coiling of the helix. A model constructed in this way, with hydrogen atoms of domain radius about 1.06 Å. determining the tightness of the helix, and hydrogen atoms of domain radius 0.78 Å. on the surface, gives an average shadow area of 35.9 sq. inches. This agrees extremely well with the observed value of 34.9 sq. Å.

Table III presents the results also for heptane and nonane. In this table the shadow areas of the models are given both for a hydrogen atom domain radius of 0.78 Å. (third power law) and for a domain radius of 0.70 Å. (fourth power law).

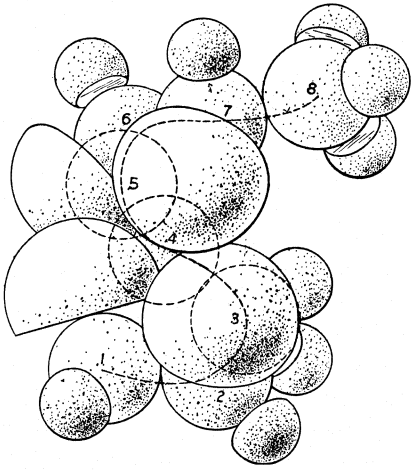

Fig. 6.

Evidently the molecules of *n*-heptane and of *n*-nonane, as well as those of *n*-octane, assume an average shape which is a loosely wound helix. If the shadow area sizes are about correct for octane, then those reported in Table III for heptane are somewhat too large, and for nonane somewhat too small, because of the fact that in the case of heptane a somewhat smaller number and in the case of nonane a somewhat larger number of hydrogen atoms share in the impact of collision.

TABLE III

COMPARISON OF COLLISION AREAS AND SHADOW AREAS FOR HEPTANE, OCTANE AND NONANE

| | Collision area, sq. Å. | Average shadow area, sq. inches | | | | | | Area of sphere of revolution of extended molecule |
|---|---|---|---|---|---|---|---|---|
| | | Tight helix | | Loose helix | | Extended | | |
| | | 0.70 Å. | 0.78 Å. | 0.70 Å. | 0.78 Å. | 0.70 Å. | 0.78 Å. | |
| *n*-Heptane | 26.7 | 23.7 | 25.2 | 30.0 | 31.1 | 34.8 | 35.9 | 93.3 |
| *n*-Octane | 34.9 | 25.0 | 26.4 | 34.5 | 35.9 | 38.7 | 40.0 | 116.8 |
| *n*-Nonane | 42.5 | 26.6 | 28.1 | 38.0 | 39.6 | 43.0 | 44.4 | 143.1 |

In the last column of Table III the cross-sectional areas of the improbable spheres of revolution of the extended molecules are listed. They are far too large to represent the actual collision areas. In so far as we have neglected the effect which end over end spin motion might have on the areas of our models, we have not disturbed in the slightest degree the validity of our general conclusions regarding the probable shape of these carbon chain molecules. Because, if the molecules are coiled up into a helix, as we have concluded that they are, rotation about the center of gravity would not appreciably affect the size, since the molecule is already approximately of spherical form. But, if the molecule were in reality extended, sufficiently rapid rotation would increase the shadow area values of the extended chain, by smearing the molecular domain over a larger space and make the decision in favor of the coiled-up form still more convincing.

In general it is to be expected that other long carbon chain molecules will coil up into loose helical forms: not only because the van der Waals forces acting between the atoms within the molecule will tend to draw the atoms closely together, and thus, in general, produce a molecular surface of minimum area, but also because the continuous punching which such a molecule suffers from its neighbors will pound it down to as compact and as closely pressed a form as rotation about chemical bonds and the special structural features of the organic molecule will permit.

Another feasible method of determining whether or not the carbon chain of a molecule such as *n*-heptane is coiled up in a helix, would involve a comparison of the collision areas (by the viscosity method) of the isomers of heptane. If the normal chain is a helix it should have very much the same collision area as the most highly branched isomers, which are already quite well bunched up into almost spherical form by their characteristic structure. Such an investigation is now under way in our laboratory.

## Summary

The viscosities of gaseous *n*-heptane, *n*-octane and *n*-nonane are determined over the temperature range 100–250°, and the Sutherland constants and collision areas of the molecules calculated. These latter are, re-

spectively, 445 and 26.7 sq. Å. for heptane, 337 and 34.9 sq. Å. for octane, 276 and 42.5 sq. Å. for nonane.

The relationship between Sutherland's constants and boiling points is discussed and it is pointed out that Vogel's empirical equation, $C = 1.47\ T_b$, can hardly be expected to hold for large molecules.

On the basis of a shadow-graphic estimation of the average cross-sectional area of plausible models of ethane, propane, butane and isobutane, and with due consideration of the spin motions of the molecules, collision areas for these molecules are predicted, which are found to be in fairly good agreement with Titani's experimental results.

By the same sort of treatment of models of heptane, octane and nonane, it is shown to be very probable that these carbon chain molecules do not exist in the extended form in the gas phase, but are coiled up on the average into the shape of a loose helix.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

# THE COLLISION AREA OF THE GASEOUS CARBON TETRACHLORIDE MOLECULE

BY ELMER H. SPERRY AND EDWARD MACK, JR.

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The recent determination by Mark and Wierl,[1] using an electron diffraction method, of the distance between the nuclei of the chlorine atoms within the gaseous carbon tetrachloride molecule makes it possible now to set up an approximate model of the carbon tetrachloride molecule, if the collision area of the molecule is known. This latter is necessary to an estimation of the size of the chlorine atom domain as conditioned by the impact of gaseous molecule collision. In the present paper the collision area of the molecule of carbon tetrachloride is determined by a gaseous viscosity method, and then the chlorine atom domain is shown to be of about the same size in the molecules of carbon tetrachloride and of chlorine. These results will be presented after the experimental procedure and data have been given.

**Experimental Procedure and Data.**—The viscosity of the vapor of carbon tetrachloride was determined with the same apparatus and in precisely the same manner already described in an accompanying paper.[2] The sample of carbon tetrachloride which was used boiled at 75.74–75.76° (742 mm.). The viscosities, $\eta$, at the several temperatures, were calculated with Meyer's transpiration formula, as before, and were corrected for slip, $\eta_c$. The results are listed in Table I.

[1] Mark and Wierl, *Naturwissenschaften*, **18**, 205 (1930).

[2] Melaven and Mack, THIS JOURNAL, **54**, 888 (1932).

TABLE I
VISCOSITIES

| Temp., °C. | $\eta$ | $\eta_0$ |
|---|---|---|
| 50 | $1.074 \times 10^{-4}$ | $1.082 \times 10^{-4}$ |
| 100 | $1.192 \times 10^{-4}$ | $1.203 \times 10^{-4}$ |
| 150 | $1.357 \times 10^{-4}$ | $1.371 \times 10^{-4}$ |
| 200 | $1.501 \times 10^{-4}$ | $1.519 \times 10^{-4}$ |
| 250 | $1.697 \times 10^{-4}$ | $1.703 \times 10^{-4}$ |

Here, as before,[2] Reynold's criterion was satisfied, that is, the flow of vapor through the capillary was slow enough to ensure viscous, and not permit turbulent, flow. From the data of Table I the Sutherland constant for carbon tetrachloride was found to be equal to 335; and the collision area, calculated from Chapman's equation, 22.0 sq. Å.

**Model and Shadow Area.**—Mark and Wierl obtained the value of about 3.14 Å. for the distance between the chlorine nuclei, which is probably more reliable than the somewhat larger result, 3.3 Å., found by Debye, Beuvilogua and Ehrhardt,[3] by x-ray examination of carbon tetrachloride vapor. Since the nuclei of the four chlorine atoms are probably spaced around the carbon atom at the four corners of a regular tetrahedron, and since the tetrahedral edge length is 3.14 Å., it can readily be calculated that the distance from the carbon nucleus to a chlorine nucleus is 1.91 Å. It only remains to estimate what size of chlorine atom domain beyond the nucleus will give a collision area of 22.0 sq. Å. Application of the shadow-graphic method, previously described, to a determination of the average cross-sectional area of a model of the carbon tetrachloride molecule shows that the radius of the chlorine atom domain (based on the average of twelve shadows) is 1.32 Å. In arriving at this result the reëntrant angles, which are small, are assumed to have no effect on the area.

However, since the molecules of carbon tetrachloride are rotating, it is necessary to consider what alteration, if any, such rotation would make in the shadow-graphic collision area. If it is assumed that the rotation is similar to that in methane, the moment of inertia is readily calculated to be $566 \times 10^{-40}$. From the equipartition of energy, then, one can calculate (approximately) that the frequency of spin at 25° would be $13.5 \times 10^{10}$ r. p. s., and the time for one complete rotation $74.1 \times 10^{-13}$ seconds. But, since both molecules sharing in the impact are spinning, and since three chlorine atoms lie around the ring of revolution, and since the whole molecule possesses also other spin motions (expressible in terms of three axes of spin), it is to be expected that the molecule would present itself as a sphere of revolution if allowed a time of about $2 \times 10^{-13}$ seconds. During such a time interval, the colliding molecule would travel through a distance of about 0.5 Å., and would probably invade to some extent the spherical envelope of revolution. If the molecule were actually able to present itself

[3] Debye, Beuvilogua and Ehrhardt, *Physik. Z.*, **30**, 84 (1929).

as a total sphere of revolution, the value of the domain radius 1.32 Å. obtained above by the shadow-graphic method on the basis that the spin effect is negligible, would have to be trimmed down to about 0.78 Å. No doubt the radius of the chlorine atomic domain, considered as a hard spherical surface, would lie somewhere between these two limits, 0.78 and 1.32 Å., nearer to the latter and possibly about 1.2 Å.

It is interesting now to compare these limits of chlorine domain size with the chlorine atom in the diatomic molecule. Two spherical atoms of chlorine telescope together to form a chemically stable molecule. The distance between nuclei is about 1.98 Å., which is the distance deduced by Elliott[4] for the normal molecule from his analysis of the absorption band spectrum of chlorine. The moment of inertia is about $113 \times 10^{-40}$ calculated for two atoms of assumed average atomic weight (35.46), rather than for isotope pairs, 35–35, 35–37, etc. The frequency of spin would average about $30.2 \times 10^{10}$ r. p. s., giving a rotational quantum number of roughly 21, which is about what is to be expected from Elliott's map of the absorption spectrum. The molecule makes a complete rotation in $33.1 \times 10^{-13}$ seconds, and in view of the facts that both colliding molecules are spinning, and that each one would have to turn through about 90°, and that each one is also spinning end over end about two axes, the molecule would require a time of about $2 \times 10^{-13}$ seconds to present itself as a sphere. During this time the colliding molecule would travel about 0.7 Å. On the whole, then, the chlorine molecule might be expected to behave less completely as a sphere of revolution than the carbon tetrachloride. If it did present itself completely as a sphere, the domain radius would have to be 0.86 Å. in order to give the observed collision area of 10.7 sq. Å. found by Rankine;[5] if the spin motion were to play a negligible part in determining the collision area, the domain radius would be about 1.44 Å.

Thus, within the limits of resolution of the present method of treatment, the conclusion may be drawn that the chlorine atom domains are of approximately the same size in the two different molecules. It is to be noted further, however, that the values given are subject to the possible errors already[2] mentioned, principally those involved in the question of the validity of the Sutherland model, and the applicability of the Chapman equation in the present situation. The questions of whether Keesom orientation occurs at impact, and of whether the velocity of the invading molecule is increased appreciably as it approaches the point of impact, are also involved.

## Summary

The viscosities of carbon tetrachloride vapor over the temperature range 50–250° have been measured. From them the Sutherland constant is

[4] Elliott, *Proc. Roy. Soc.* (London), **A127**, 638 (1930).

[5] Rankine, *ibid.*, **A98**, 373 (1921).

calculated to be 335, and the collision area of the carbon tetrachloride 22.0 sq. Å.

The conclusion is drawn that the atomic domain size of the chlorine atom is roughly the same in the gaseous molecules of carbon tetrachloride and chlorine.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE INORGANIC CHEMISTRY LABORATORY, PURDUE UNIVERSITY]

# OXYCYANOGEN. II. THE FREE RADICAL

BY HERSCHEL HUNT

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Of the eight halogenoid free radicals $(CN)_2$, $(SCN)_2$, $(SeCN)_2$, $(SCSN_3)_2$, $N_3$, $(TeCN)_2$, $(ONC)_2$ and $(OCN)_2$, the latter four have not been isolated or satisfactorily described. The author[1] has failed to check the work of Lidov. A compound of carbon, oxygen and nitrogen such as he describes was not found.

Birckenbach and Linhard[2] treated silver cyanate with iodine in ligroin, carbon tetrachloride, ethyl chloride, benzene and ether solutions at $-20°$ and obtained a product which they describe as IOCN. They state that it is impossible to obtain $(OCN)_x$ by this process. $(SCN)_2$ and $(SeCN)_2$ have been prepared in a similar manner by Söderbäck[3] and Kaufmann,[4] respectively.

It is the purpose of this paper to describe the isolation and properties of $(OCN)_x$.

## Preparation

Fresh silver cyanate was prepared by precipitation from potassium cyanate and silver nitrate. The salt was carefully washed and dried. Analytical tests showed it to be free from any unchanged silver nitrate or oxidizing material. The salt was carefully dried over sulfuric acid in the dark to prevent decomposition.

The solvents which proved satisfactory for use were carbon disulfide and carbon tetrachloride. Several other common solvents, ether, alcohols and acetone, were tried but all gave difficulties of hydrolysis or side reactions. The solvents were thoroughly dried over soda lime and fractionally distilled before use.

Resublimed iodine was dissolved in the carbon tetrachloride or carbon disulfide to make a 0.05 normal solution. Greater concentrations do not react as rapidly. This solution was stirred in a mercury-sealed stirrer at room temperature for sixty days with a large excess of silver cyanate. No gas is given off but the iodine slowly disappears. This would indicate

$$2AgCNO + I_2 = AgI + (CNO)_2 \text{ or}$$
$$AgCNO + I_2 = AgI + IOCN$$

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[1] H. Hunt, THIS JOURNAL, **53**, 2111 (1931).

[2] Birckenbach and Linhard, *Ber.*, **62**, 2261 (1929); **63**, 2544 (1930); **64**, 961 (1931); **64**, 1076 (1931).

[3] Söderbäck, *Ann.*, **419**, 217 (1919).

[4] Kaufmann and Kögler, *Ber.*, **59**, 178 (1926).

When the solution became colorless, *i. e.*, when the iodine had all reacted, the stirring was stopped and the mixture examined. Since the silver cyanate was not dissolved, the silver iodide was formed only on the surface and a large percentage of the silver cyanate was left unchanged. The yellow precipitate was filtered off and treated with nitric acid. The silver cyanate decomposed leaving silver iodide corresponding to the amount of iodine consumed: g. of iodine added, 8.8, 8.0 and 6.0; g. of silver iodide found, 16.3, 14.7 and 11.1, respectively.

The colorless carbon disulfide solution behaves as follows. (1) On chilling to 0 to $-10°$ a white solid separates. The white solid evaporates when the solution is left on a watch glass. While filtering off the silver iodide and silver cyanate a white solid crystallized around the top of the funnel. (2) The solution liberates iodine from potassium iodide but will not displace bromine. The liberation is faster if the solution is placed in the sunlight, indicating that we have a polymer which reacts slowly and not $CNO^-$. (3) The solution gives a white precipitate with $Ag^+$ or $Ba^{++}$; the precipitate is decomposed with dilute nitric acid. (4) The solution is stable when heated in a closed tube to 100°. (5) The solution can be concentrated by distillation, the distillate being richer in oxycyanogen than the residue. If the solution is subjected to a vacuum it soon loses its oxidizing power. (6) Decomposition of the solution gave no trace of iodine, the interhalogen-halogenoid, IOCN, being thought of as one possibility. (7) The Beilstein test showed the solution to be free of any halogen. Iodine could not be displaced by stronger oxidizing agents such as chlorine or sulfuric acid.

The reaction goes faster in carbon disulfide than in carbon tetrachloride. An alcoholic solution reacts readily at room temperature but as soon as the silver iodide is filtered off the solution begins to decompose and iodine is liberated. The clear solution is a very strong oxidizer. The fresh solution probably contains IOCN.

Attempts to combine cyanogen with activated oxygen only resulted in hazardous explosions.

## Analysis

The amount of $(OCN)_x$ present in a given volume of solution was determined by the liberation of iodine. (See Kaufmann and Gaertner's work on thiocyanogen.)[5]

$$(OCN)_2 + 2KI + 2H_2O + 2H_2SO_4 = K_2SO_4 + (NH_4)_2SO_4 + I_2 + 2CO_2$$

The steps of hydrolysis and reaction are presumably the same as those given for $(SCN)_2$ by various authors.[5,6]

The composition was determined by the method of Herting.[7] $(CNO)_x$ in dilute hydrochloric acid decomposes, giving ammonium chloride and carbon dioxide. The solution is then transferred to a distilling flask, made alkaline and the ammonia distilled into a standard acid. The acid is then back titrated with alkali, methyl orange being used as an indicator: grams of $(CNO)_x$ present in solution as computed from iodine liberated, 0.1428, 0.1260 and 0.1470; % $N_2$ found, 33.30, 32.70 and 32.86; average, 32.95; % $N_2$ calcd., 33.33. Equal amounts of the same solution were used for the iodine liberation and the nitrogen determination. Attempts were made to

[5] Kaufmann and Gaertner, *Ber.*, **57**, 928 (1924).

[6] Bjerrum and Kirschner, *Kgl. Dansk. Videnskab. Selskab.* [8] **I**, 76 (1918); Lecher, Wittwer and Speer, *Ber.*, **56**, 1104 (1923).

[7] Herting, *Z. angew. Chem.*, **24**, 585 (1901).

determine the molecular weight but the properties of $(CNO)_x$ and experimental difficulties prevent the report of a molecular weight. $(CNO)_2$ is used only by analogy to $(SCN)_2$.

When the carbon disulfide solution of the cyanate is chilled, the white flake-like crystals which appear contain carbon disulfide. The white plates were purified by repeated fractionation. The purified crystals (plates) were found to melt at $-12 \pm 0.5°$. The $(OCN)_x$ decomposes quickly at room temperature when free from solvent.

Birckenbach[8] found a secondary product in his solutions at $-20°$. However, he obtained mainly IOCN. Since the author could not obtain $(OCN)_x$ in ether or alcoholic solutions, the two authors are now agreed. The reaction in carbon disulfide and carbon tetrachloride probably takes place in two steps

$$AgCNO + I_2 = AgI + IOCN$$
$$AgCNO + IOCN = AgI + (CNO)_2$$

different temperatures and solvents changing the end-product of the reaction. Birckenbach did not use an excess of silver cyanate.

Birckenbach and Kellermann[9] report that in electrolyzing an alcoholic solution of potassium cyanate they obtained an anode solution which will liberate iodine from potassium iodide and will react with copper, zinc and iron without gas evolution. They explain their results as follows

$$2OCNK = 2K + (OCN)_2;\ CH_3OH + (OCN)_2 = HCHO + 2OCNH;$$
$$OCNH + CH_3OH = NH_2COOCH_3;\ \text{and}\ NH_3COOCH_3 + OCNH = NH_2CONHCOOCH_3$$

Careful repetition of this work did not yield an oxidizing solution when the alcohol was kept absolutely dry. The methyl alcohol was purified as described by Hunt and Briscoe[10] for conductivity purposes. Birckenbach's apparatus was modified so as to eliminate any possibility of water being carried back with the mercury. The mercury was cleaned and dried each time before it was poured through the cathode chamber (see their description of apparatus). However, if a trace of water is added to the solution, just such a solution as they describe will be obtained. The author suggests the following explanation, which has been accepted by Birckenbach: $2KOCN = 2K\ (amalgam) + 2OCN^- - 2E$; $CH_3OH = HCHO + 2H^+ + 2E$; and $2H^+ + 2OCN^- = 2HOCN$, or if water is present the following: $HOH + 2OCN^- = HOCN + HO_2CN + 2E$.

Birckenbach writes that no precautions were taken to keep the solution anhydrous. Cyanic acid and formaldehyde were found in the alcoholic anode solution in large amounts. Hydrogen is not liberated at the cathode in water solution. This latter equation is in agreement with the hydrolysis of oxycyanogen. The electrolysis was then performed in an aqueous

[8] Birckenbach, private communication.

[9] Birckenbach and Kellermann, *Ber.*, **58**, 786 (1925).

[10] H. Hunt and H. T. Briscoe, *J. Phys. Chem.*, **33**, 1495 (1929).

solution. Much larger yields of the oxidizing material were easily obtained by this method. The anode solution deposits white crystals on evaporation. A solution of the crystals shows oxidizing powers but this property is destroyed on warming the solution. The compound will oxidize methyl alcohol to formaldehyde. Further investigation is being made to determine whether the oxidizing material is a percyanic acid, $HO_2CN$.

## Summary

1. $(OCN)_x$, the free oxycyanogen radical, has been isolated and some of its properties determined.

2. An explanation is offered for the oxidizing solution obtained on the electrolysis of potassium cyanate.

LAFAYETTE, INDIANA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 685, AND OF VASSAR COLLEGE]

# THE QUINHYDRONE ELECTRODE. IV

BY OLIVE M. LAMMERT AND J. LIVINGSTON R. MORGAN

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## Introduction

While a number of investigators have made determinations of the electromotive force developed between the quinhydrone and other standard half-cells in solutions other than 0.1 *M* hydrochloric acid, we have found no data which indicate that any extended study has been made of the effect of the composition and concentration of the solution on the reproducibility of the quinhydrone electrode itself.

Biilmann[1] tested the electrode in a number of dilute solutions ranging in $P_H$ from 1 to 9 and compared the data with results from conductance and other measurements, with which they usually agreed to about 0.1–0.003 $P_H$. S. P. L. and M. Sörensen and Linderström-Lang[2] made a study of the inherent salt error of the quinhydrone electrode and pointed out that while the quinhydrone electrode gave the same values as the hydrogen electrode in solutions containing little or no salt it did not give the same value in solutions containing large amounts of salt or in strong acid solutions. This they explained by assuming that the electrolyte content so changed the activity ratio of quinone to hydroquinone that the potential difference measured is no longer the measure of the hydrogen-ion concentration but must be corrected by a factor other than one. Their measurements, like Kolthoff's,[3] who also wrote on the reliability of the quinhydrone electrode for the measurement of hydrogen-ion concentration

[1] Biilmann, *Ann. chim.*, [9] **15**, 109 (1921).

[2] S. P. L. Sörensen, M. Sörensen and Linderström-Lang, *ibid.*, [9] **16**, 283 (1921).

[3] Kolthoff, *Z. physiol. Chem.*, **144**, 259 (1925).

in various solutions, were reported to only 0.0001 volt and involved the reproducibility of the hydrogen electrode as well. In view of the fact that we had found such excellent reproducibility under certain optimum conditions in 0.1 *M* hydrochloric acid[4] and in view of the fact that no work has been done, so far as we know, on the reproducibility of the quinhydrone electrode itself in salt and in other acid solutions which would enable one to know how much of the error pointed out by Sörensen was constant, as assumed by him, and how much was due to an effect on the reproducibility of the electrode, we extended our study to solutions other than hydrochloric acid.

## Procedure and Results

For this work we selected representative electrodes from those upon which we have reported previously, electrodes of C. P. platinum, 24 K gold and lead pencil graphite of different sizes. These electrodes had been used so often in 0.1 *M* hydrochloric acid that their characteristic behavior was well known and was further tested by frequent measurements in 0.1 *M* hydrochloric acid between measurements in other solutions. With the electrodes controlled in this way we felt it unnecessary to make as large a number of measurements on each electrode as we had made in the earlier part of the work or to use as many electrodes of each series, or as many series.

The solutions used are listed in the first column of the tables. In general, solutions were selected in the range of $P_H$ and for the concentrations at which the electrode was supposedly applicable. Recrystallized potassium chloride was used and the grade of phosphates was that sold by the LaMotte Chemical Company for buffers.

The method and apparatus have been described in the first papers of this series. We have been able to test one part of our technique which was mentioned in the third paper as a possible source of error, namely, that in intercomparisons of electrodes in the same vessel there is the possibility, if a reaction is catalytic in nature, that a small electrode will be affected by the presence in the vessel of a large electrode. Although we have made a large number of comparisons of the same electrodes in all types of combinations, we can find no effect of one upon the other except in the case of the arc carbons already mentioned. A group of electrodes of one kind and series measured in one beaker gave the same average potential differences, ranges and deviations as the same electrodes measured in several beakers containing electrodes of the widest differences in sizes, compositions and properties.

The results for the reproducibility of the different types of electrodes in different solutions stirred in air are given in Table I. The values for

[4] Morgan, Lammert and Campbell, THIS JOURNAL, **53**, 454, 597 (1931); Morgan and Lammert, *ibid.*, 2154 (1931).

0.1 *M* hydrochloric acid, previously reported, are included for comparison. In the first column are given the solutions used, in the second, third and fourth the values for one series of electrodes, in the fifth, sixth and seventh the values for another series. The second and fifth columns contain the values for the average potential difference in microvolts, an average obtained, as explained in the first paper of this series, from a number of values taken after the electrodes had been immersed in the solution for at least an hour. The third and sixth columns contain the values for the range of potential differences observed, also in microvolts, and the fourth and seventh columns the values for the average deviation from the average

TABLE I

COMPARISON OF THE POTENTIAL DIFFERENCES

Obtained after sixty minutes in solutions of various compositions saturated with quinhydrone between electrodes made of C. P. platinum, 24 K gold, and lead pencil graphite of different sizes. Solutions stirred in presence of air; electrodes short-circuited and dried in air.

| Solutions | Electrodes: Pt, Nos. 1–4 Av. P. D., μ v. | Range, μ v. | Av. dev., μ v. | Electrodes: Au, Nos. 1–4 Av. P. D., μ v. | Range, μ v. | Av. dev., μ v. |
|---|---|---|---|---|---|---|
| 0.1 *M* HCl | 10 | 88 | 7 | 12 | 66 | 10 |
| .01 *M* HCl and 0.09 *M* KCl | 3 | 13 | 2 | 4 | 15 | 3 |
| .1 *M* KCl | 46 | 110 | 36 | 283 | 990 | 267 |
| .34 *M* KCl | 51 | 330 | 64 | 13824 | 25900 | 9268 |
| .1 *M* $HNO_3$ | 6 | 14 | 4 | 8 | 21 | 5 |
| .1 *M* $HC_2H_3O_2$ | 36 | 130 | 24 | 30 | 107 | 18 |
| .1 *M* $HC_2H_3O_2$ and 0.1 *M* $NaC_2H_3O_2$ | 26 | 200 | 19 | 6 | 22 | 5 |
| .1 *M* $HC_2H_3O_2$ and 0.75 *M* $NaC_2H_3O_2$ | 9 | 34 | 6 | 30 | 99 | 26 |
| .05 *M* $H_2SO_4$ | 17 | 51 | 10 | 11 | 64 | 10 |
| .03 *M* $Na_2HPO_4$ and 0.04 *M* $KH_2PO_4$ | 40 | 128 | 25 | 35 | 125 | 29 |
| .3 *M* $Na_2HPO_4$ and 0.4 *M* $KH_2PO_4$ | 8 | 18 | 5 | 8 | 21 | 6 |
| | Electrodes: 4B, Nos. 1–4 | | | Electrodes: L and N, Nos. 1–4 | | |
| 0.1 *M* HCl | 5 | 33 | 5 | 1 | 8 | 1 |
| .01 *M* HCl and 0.09 *M* KCl | 31 | 150 | 31 | 3 | 10 | 2 |
| .1 *M* KCl | 246 | 870 | 222 | 141 | 360 | 101 |
| .34 *M* KCl | 403 | 1200 | 303 | 165 | 570 | 155 |
| .1 *M* $HNO_3$ | 9 | 53 | 6 | 10 | 26 | 9 |
| .1 *M* $HC_2H_3O_2$ | 79 | 541 | 80 | 22 | 82 | 14 |
| .1 *M* $HC_2H_3O_2$ and 0.1 *M* $NaC_2H_3O_2$ | 28 | 230 | 28 | 14 | 23 | 6 |
| .1 *M* $HC_2H_3O_2$ and 0.75 *M* $NaC_2H_3O_2$ | 27 | 90 | 27 | 35 | 48 | 4 |
| .05 *M* $H_2SO_4$ | 9 | 34 | 6 | 20 | 54 | 15 |
| .03 *M* $Na_2HPO_4$ and 0.04 *M* $KH_2PO_4$ | 292 | 926 | 221 | 44 | 130 | 40 |
| .3 *M* $Na_2HPO_4$ and 0.4 *M* $KH_2PO_4$ | 17 | 63 | 16 | 15 | 33 | 11 |

TABLE I (*Concluded*)

| Solutions | Electrodes: $P_{11}$, Nos. 1–4 Av. P. D., μ v. | Range, μ v. | Av. dev., μ v. | Electrodes: $G_{11}$, Nos. 1–4 Av. P. D., μ v. | Range, μ v. | Av. dev., μ v. |
|---|---|---|---|---|---|---|
| 0.1 *M* HCl | 4 | 18 | 3 | 6 | 15 | 4 |
| .01 *M* HCl and 0.09 *M* KCl | 1 | 13 | 2 | 3 | 5 | 2 |
| .1 *M* KCl | 31 | 67 | 17 | 23 | 67 | 20 |
| .34 *M* KCl | 16 | 39 | 13 | 750 | 2618 | 564 |
| .1 *M* $HNO_3$ | 2 | 8 | 2 | 11 | 25 | 4 |
| .1 *M* $HC_2H_3O_2$ | 6 | 27 | 4 | 23 | 80 | 17 |
| .1 *M* $HC_2H_3O_2$ and 0.1 *M* $NaC_2H_3O_2$ | 4 | 20 | 4 | 9 | 17 | 3 |
| .1 *M* $HC_2H_3O_2$ and 0.75 *M* $NaC_2H_3O_2$ | 3 | 14 | 3 | 8 | 26 | 7 |
| .05 *M* $H_2SO_4$ | 4 | 9 | 2 | 7 | 20 | 4 |
| .03 *M* $Na_2HPO_4$ and 0.04 *M* $KH_2PO_4$ | 16 | 68 | 8 | 40 | 188 | 37 |
| .3 *M* $Na_2HPO_4$ and 0.4 *M* $KH_2PO_4$ | 26 | 90 | 22 | 22 | 59 | 20 |
| | Electrodes: $P_{13}$, Nos. 1–4 | | | Electrodes: $G_{13}$, Nos. 1–4 | | |
| .01 *M* HCl and 0.09 *M* KCl | 8 | 27 | 4 | 2 | 7 | 2 |

value given in the second and fifth columns. No direction of the deviation is indicated since the electrodes in any one series are supposedly identical and could not be distinguished from one another except by our arbitrary system of numbering; hence the signs are unimportant in this table.

It will be observed that for all of the electrodes except the special gold wires from Leeds and Northrup (L and N) the average potential differences are about the same for the three stronger acids, hydrochloric, nitric, and sulfuric, although the ranges and average deviations vary somewhat, and are smaller for the platinum foils ($P_{11}$) than for the other electrodes. The behavior of the L and N electrodes in nitric and in sulfuric acids is surprising in view of the fact that they had given such consistently low results in hydrochloric acid, but could be accounted for only as affected by the particular acids since the electrodes were frequently tested in hydrochloric acid between measurements in other acids and found to give the same characteristic low values. In acetic acid, however, the average potential differences, ranges and deviations are larger for all of the electrodes, though very little larger for the platinum foils $P_{11}$, which incidentally have given consistently better results throughout the measurements in all of the acids than any of the other electrodes reported upon in this paper except the L and N in hydrochloric acid. Moreover, the measurements in 0.1 *M* acetic acid gave rather wide ranges on the potentiometer over which there was no deflection of even our 2285 A Leeds and Northrup galvanometer. This fact suggested that the internal resistance of the cell was becoming appreciable in the case of the acetic acid and that precise measurements can no longer be made in solutions of

such high resistance unless a more sensitive galvanometer is used or the current amplified, or large platinum electrodes used. It will be recalled that in our earlier work platinum electrodes of a given size seemed to give higher current capacities than gold electrodes of the same size.

All in all, then, we are of the opinion, in view of these data and in view of other data we have in other acids and in other concentrations, data which were obtained under slightly different conditions not strictly comparable and hence not included in the table, that the quinhydrone electrode can be reproduced with great precision in solutions of all the common mineral acids, hydrochloric, nitric, sulfuric and phosphoric and in acetic acid in concentrations 0.1 *M* or less, the degree of precision being determined by the sensitiveness of the galvanometer. In a given conductance cell the resistance of the solutions we were using at the time, 0.1 *M* hydrochloric, 0.1 *M* nitric, 0.05 *M* sulfuric, 0.05 *M* hydrochloric, 0.025 *M* sulfuric, 0.033 *M* phosphoric, 0.1 *M* acetic and 0.05 *M* acetic were 39.5, 42, 62, 79, 116, 298, 3006 and 4311 ohms, respectively, and the approximate $P_H$ of the solutions 1.04, 1.09, 1.22, 1.36, 1.47, 1.96, 2.88 and 2.95, respectively. That it is with the increasing resistance that the precision decreases rather than with the increasing $P_H$ seems probable in view of the fact that when a moderate amount of sodium acetate (approximately 0.1 mole) is added to the 0.1 *M* acetic acid solution, decreasing the resistance to 208 ohms but increasing the $P_H$ to 4.59, the average potential differences and the range of no deflection on the galvanometer both decrease. An even greater decrease is observed with the platinum electrodes when more sodium acetate (approximately 0.75 mole) is added to the same 0.1 *M* acid solution, a procedure which brings the resistance of the solution to that of the 0.1 *M* hydrochloric (39 ohms) but raises the $P_H$ of the solution to 5.52. The value does not change greatly with the graphite or with the gold foil but increases with the other gold electrodes. As we shall see, this is quite consistent with the observations on the stronger salt solutions which we shall discuss presently.

The 0.01 *M* hydrochloric acid and 0.09 *M* potassium chloride mixture suggested by Veibel[5] as a suitable solution for a standard electrode gave consistently low average potential differences and ranges for all the electrodes except the graphite.

The results with phosphoric acid have been discussed and present no special problems in reproducibility. The so-called Sörensen's phosphate mixture with a $P_H$ of 6.53, approximately 0.03 *M* in $Na_2HPO_4$ and 0.04 *M* in $KH_2PO_4$, having a resistance in our cell of 276 ohms, was used and gave average potential differences rather higher than any of the acids tested, but about the same for all of the electrodes, except graphite and platinum foils. Graphite gave exceptionally high results, platinum lower than

[5] Veibel, *J. Chem. Soc.*, **123**, 2203 (1923).

the other electrodes but higher than in the acids. When, however, the weights per liter of phosphate were increased approximately tenfold, but kept in the same proportion, with the result that the mixture had a resistance of 39 ohms, that of the 0.1 *M* hydrochloric, but a $P_H$ approximately the same as the first mixture, the average potential differences decrease with all of the electrodes except the platinum foils.

The results in 0.1 and 0.34 *M* potassium chloride are by far the most interesting. Here we have unbuffered neutral solutions of resistances 122 and 39 ohms, respectively, in contrast to the other solutions which have been either acid or buffered. In the first place, in the 0.1 *M* solution all the results are higher than those in the 0.1 *M* hydrochloric acid. When the resistances of the solutions are made comparable by adding potassium chloride until the solution is 0.34 molar, the results show even greater discrepancies. In the first place, the platinum electrodes stand out as giving distinctly lower results, second, the gold electrodes and particularly the smallest gold wires give amazingly high results, and, third, the graphite gives results somewhere between the platinum and gold. Of course, these results were immediately suspected and the electrodes thoroughly examined but no reason could be found for their behavior other than the fact that unbuffered solutions in the neutral range not only give constant errors when the quinhydrone electrode is used, due to the fact that the hydrogen ion from the dissociation of hydroquinone becomes appreciable, but also that the reproducibility, particularly with the gold electrodes, is affected. All the electrodes gave rather large ranges on the potentiometer over which there was no deflection, the platinum again being better in this respect than the gold. The reproducibility for electrodes used in these solutions is so poor that the actual differences are of no value.

An intercomparison of the potential differences developed by electrodes of the series recorded in Table I was made, of which the results given in Table II are typical. As stated in a previous communication such an intercomparison gives some idea of the accuracy which can be obtained by different investigators using different electrode substances from different sources. The signs of the potential differences of the cells are reported in this table as in the third paper of the series, since, while two metals may give the same reproducibility among different pieces of the same sample, it is of course interesting to see whether the same potential difference is developed in the two cases. As stated in the third paper the sign is given to the first mentioned electrode; when the average deviation is of the same order of magnitude as the average potential difference it seems probable that a sign in any one direction does not represent an actual difference of potential developed but merely a deviation, but when the average potential difference is in one direction and is larger than the average deviation, it seems probable that there is an actual difference developed by the two metals.

TABLE II

COMPARISON OF THE POTENTIAL DIFFERENCES

Obtained after sixty minutes in various solutions saturated with quinhydrone between electrodes from different series made from substances of different composition and sizes. Solutions stirred in air. Electrodes dried and short-circuited.

| Solutions | Electrodes: $Pt_{1-4}$ vs. $Au_{1-4}$ Av. P. D., $\mu$v. | Range, $\mu$v. | Av. dev., $\mu$v. | Electrodes: $Pt_{II}$ vs. $Au_{II}$ Av. P. D., $\mu$v. | Range, $\mu$v. | Av. dev., $\mu$v. |
|---|---|---|---|---|---|---|
| 0.1 *M* HCl | ±15 | 30 | 6 | .. | .. | .. |
| .01 *M* HCl and 0.09 *M* KCl | +27 | 42 | 5 | ± 5 | 14 | 3 |
| .1 *M* KCl | ±36 | 80 | 22 | ±86 | 200 | 58 |
| .34 *M* KCl | +8726 | 21920 | 8553 | ±219 | 970 | 218 |
| .1 *M* $HNO_3$ | +31 | 48 | 7 | ± 8 | 27 | 8 |
| .1 *M* $HC_2H_3O_2$ | +79 | 177 | 27 | ±11 | 33 | 8 |
| .1 *M* $HC_2H_3O_2$ and 0.1 *M* $NaC_2H_3O_2$ | +47 | 65 | 9 | ± 5 | 11 | 3 |
| .1 *M* $HC_2H_3O_2$ and 0.75 *M* $NaC_2H_3O_2$ | +28 | 58 | 14 | ± 3 | 9 | 2 |
| .05 *M* $H_2SO_4$ | +40 | 75 | 16 | ± 7 | 17 | 4 |
| .03 *M* $Na_2HPO_4$ and 0.04 *M* $KH_2PO_4$ | +64 | 82 | 12 | ±73 | 153 | 23 |
| .3 *M* $Na_2HPO_4$ and 0.4 *M* $KH_2PO_4$ | +53 | 70 | 14 | +81 | 132 | 19 |

These results should be compared with those in Table I. In general the same solutions which gave difficulty in reproducibility when different pieces of the same metal were used gave difficulty in that high differences in potential were developed when electrodes of different kinds or sizes were coupled to form cells. In the neutral unbuffered solutions the same characteristic high values appeared whenever gold electrodes were involved. Again, in general, the larger the electrode, the smaller the differences and average deviation.

In conclusion, then, these results seem to indicate that while the quinhydrone electrode is reproducible with great precision in 0.1 *M* hydrochloric acid and in dilute solutions of other mineral acids, particularly if platinum foil electrodes of at least 1 × 1 sq. cm. surface are used, its reproducibility in other solutions and particularly in neutral salt solutions is largely a matter of conjecture and seems in some way to depend upon the substance used as the base of the electrode. With small gold electrodes differences in potential were observed between two pieces of the same wire immersed in the same solution, which were far greater than the salt error correction suggested by Sörensen for like concentrations of similar solutions, corrections deduced from solubility measurements and assumed to be the "constant error" of the electrode in such solutions. Saturated solutions of quinhydrone in these different electrolytes were placed in stoppered tubes and kept for some days. In all cases there was about the same amount of undissolved quinhydrone in the bottom of the tube but, while the 0.1 and 0.05 *M* hydrochloric, 0.1 *M* nitric, 0.1 and 0.05 *M* sulfuric acids

and the 0.1 and 0.34 *M* potassium chloride and 0.01 *M* hydrochloric acid and 0.09 *M* potassium chloride mixture all gave solutions which were only slightly darker than the original mixtures, the 0.033 *M* phosphoric and acetic acids and the strong phosphate buffer gave solutions somewhat darker. Next in intensity of color were the more dilute mixtures of phosphates and the more dilute acetate and acetic acid mixtures and then finally the more concentrated acetate–acetic acid mixtures. After three days the acetate and phosphate mixtures with quinhydrone were almost black, the acetate solutions having turned first. Apparently then there is no very obvious connection between the reproducibility of the electrode and the well-known darkening of quinhydrone solutions. As a matter of fact better reproducibility was obtained in 0.1 *M* sodium hydroxide solutions than in the potassium chloride solutions measured, although quinhydrone solutions turn black instantly when sodium hydroxide is added in excess. About the only generalization which can be made as the result of this study is that while the quinhydrone half-cell prepared in 0.1 *M* hydrochloric or solutions of other strong acids, or in the mixture suggested by Veibel, 0.01 *M* hydrochloric acid and 0.09 *M* potassium chloride, is reproducible with such precision that it recommends itself highly as a secondary standard, it must be used with great discretion as a working electrode in other solutions. Since the electrode material itself is apparently not "inert," as assumed by its early discoverers and advocates, but seems to play some role, whether catalytic or of another nature, its composition must be considered carefully with particular reference to the solution and the conditions under investigation. The use of the half-cell in any research ought to be preceded by a study of its reproducibility under the conditions demanded by the research. The simplicity of its preparation, its constancy and accuracy in some solutions and the unsubstantiated statements in the literature concerning the interchangeability of gold or platinum as electrode material make it an extremely dangerous tool in the hands of the inexperienced. While a number of explanations suggest themselves to account for these variations in application, any final conclusions will be deferred until the work in nitrogen and oxygen is completed.

We are greatly indebted to the special Research Fund of Columbia University for a grant for this work and to Miss Margaret Campbell, who, as research assistant, made the measurements for this paper.

## Summary

The reproducibility of the quinhydrone electrode prepared with platinum, gold and graphite has been studied in 0.05 and in 0.1 *M* hydrochloric acid, in a mixture of 0.01 *M* hydrochloric acid and 0.09 *M* potassium chloride, in 0.1 *M* and in 0.34 *M* potassium chloride, in 0.1 *M* nitric acid, in 0.1 *M* acetic acid, in a mixture of 0.1 *M* acetic acid and 0.1 *M* sodium

acetate, in another 0.1 *M* acetic acid and 0.75 *M* sodium acetate, in 0.025 *M* and 0.05 *M* sulfuric acid, in 0.033 *M* phosphoric acid, in a mixture of 0.03 *M* dibasic sodium phosphate and 0.04 *M* monobasic potassium phosphate and in a mixture of 0.3 *M* dibasic sodium and 0.4 *M* monobasic potassium phosphates, and the following conclusions drawn.

1. The quinhydrone half-cell may be prepared in dilute solutions of the common mineral acids with precision comparable to that obtained in 0.1 *M* hydrochloric acid, particularly if platinum foil electrodes are used and the resistance of the solution is not too high.

2. The quinhydrone half-cell has been prepared in acetate and phosphate buffer solutions of $P_H$ values approximately 4.6–5.0 and 6.1–6.5, respectively, with a fair degree of precision, the average potential differences between two like electrodes in these solutions being about ten times as large as the corresponding averages in 0.1 *M* hydrochloric acid.

3. In unbuffered salt solutions in the neutral range the quinhydrone electrode is likely to give extremely erratic results, particularly if gold or graphite electrodes are used. The error, due to lack of reproducibility, may be far greater than any constant error calculated by Sörensen and described as "salt error."

4. The role of the electrode substance in the quinhydrone half-cell cannot be overlooked and must be tested for each particular system in which the electrode is to be used.

5. The results in this paper indicate that while the quinhydrone half-cell makes an excellent secondary standard, since it gives extremely precise results when the conditions can be made optimum, it must be used with great discretion as a working electrode, its use being preceded by a study of its reproducibility in the system under investigation.

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# THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF SILVER CHLORIDE AND SODIUM CHLORIDE

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Extremely little complete thermodynamic information is available concerning solid salts and their solid solutions. Where so many of these crystals have been examined by the methods of x-ray analysis and their lattice arrangements in many cases satisfactorily established, the possibility of correlating the space lattice data with the thermodynamic properties, especially of solid solutions, is a very attractive one.

The galvanic cell has been employed to furnish a great mass of valuable data which permit the calculation of important thermodynamic quantities for aqueous solutions of salts. Little attention has been paid to the possibility of constructing such cells with the pure crystalline salt or its solid solutions as electrolyte. Haber and Tolloczko,[2] Katayama,[3] and Reinhold[4] have shown that this type of cell can be constructed for certain simple systems, and that their electromotive force can be determined by the usual varieties of electrical equipment. Unfortunately, the presence of unknown potentials between electrolytes in many of their cells prevents precise thermodynamic calculations.

In considering the properties of any material which is to be employed as the electrolyte in a reversible galvanic cell, in addition to the chemical considerations concerning the cell reaction, it is necessary to be certain that the conduction processes through the material are entirely ionic, that Faraday's law of electrolysis is obeyed, and that the diffusion of ions is sufficiently rapid to avoid the uncertainties of cumulative polarization effects produced by the passage of small currents in the experimental determination of the electromotive force. Aqueous solutions of salts, if not too dilute, as well as fused salts, completely fulfil these requirements. However, for non-aqueous salt solutions and for solid salts these considerations become important factors in the choice of materials. We have satisfactory proof of a transfer of charges by the transfer of matter according to Faraday's law. Tubandt and his co-workers[5] quantitatively checked Faraday's law on silver chloride, silver bromide, silver

[1] National Research Fellow in Chemistry.

[2] Haber and Tolloczko, *Z. anorg. Chem.*, **41,** 407 (1904).

[3] Katayama, *Z. physik. Chem.*, **61,** 566 (1908).

[4] Reinhold, *Z. anorg. allgem. Chem.*, **171,** 181 (1928).

[5] Tubandt and co-workers, *Z. physik. Chem.*, **87,** 513, 543 (1914); *Z. anorg. allgem. Chem.*, **110,** 196 (1920); **115,** 105 (1921); **117,** 1, 48 (1921); **160,** 222, 297 (1927); **165,** 195 (1927).

iodide, lead chloride, lead fluoride, silver sulfide and cuprous sulfide. A transfer of matter by the current was found for a large number of different solid halides, nitrates, sulfates and even for lithium hydride.[6] There is no doubt that in all of these substances we have to do with an ionic conductivity following the Faraday law for electrolytes. Bruni,[7] Fraenkel and Houben,[8] and Vegard[9] have shown that diffusion processes in crystalline solids may be very rapid even at temperatures well below the melting point.

This research is a part of an extensive program now in progress involving the experimental determination of the procedure and technique necessary for the construction and manipulation of reversible cells containing solid electrolytes.

## Experimental Considerations

The cell studied in this research can be represented by $Pb/PbCl_2/-AgCl, NaCl, Ag$, where all the materials are solid, and sodium chloride is present in solid solution with silver chloride. The cell reaction is

$$Pb(s) + 2AgCl_{(solution)} = PbCl_2(s) + 2Ag(s)$$

The mechanism whereby this reaction may take place is entirely analogous to that for the aqueous cell $Pb/PbCl_2(aq.)/AgCl(s), Ag$, the silver–silver chloride electrode playing a similar role in both. To avoid the uncertainties of a transference potential across the interface $AgCl/PbCl_2$, it is necessary to place the silver electrode in contact with both the silver chloride and the lead chloride. When a small negative current passes through the cell from right to left, silver ions which are present in the lead chloride in small concentrations and in equilibrium with the solid solution are discharged at the silver electrode. Chloride ions traverse the lead chloride to form more lead chloride with the lead ions which are produced at the lead electrode. A reversal of the current reverses this process.

Cells must be free from vitiating factors such as side reactions at the electrodes due to the reaction of the electrode with the electrolyte or to the cell reaction taking place at the electrodes themselves. For example, in the cell studied in this research, silver must not react with lead chloride or sodium chloride, and lead must not reduce lead chloride. In addition, silver and sodium chlorides must not react with or be soluble in lead chloride. The melting points of all the salts should fall within an experimentally convenient range. For this system all of these conditions are fulfilled. Silver chloride forms a complete series of solid solutions with

[6] Peters, *Z. anorg. allgem. Chem.*, **131**, 140 (1923).
[7] Bruni, *Chem. Reviews*, **1**, 345 (1925).
[8] Fraenkel and Houben, *Z. anorg. allgem. Chem.*, **116**, 1 (1921).
[9] Vegard, *Z. Physik*, **5**, 393 (1921).

sodium chloride.[10] Lead chloride gives a simple eutectic with silver chloride[11] and sodium chloride,[12] at temperatures of 310 and 410°, respectively.

In order to prepare a homogeneous solid solution the fused salt mixture must be cooled rapidly and then annealed for a long time just below its melting point. Crystalline materials may exhibit slight differences of thermodynamic behavior due to strains. The higher the temperature and the softer the substance the less the magnitude of these effects.[13]

**Materials and Apparatus.**—The silver wire and lead used in this research were of the highest purity obtainable from commercial sources. These substances were used without further purification. Lead chloride was freed from moisture and hydrolysis products by fusing and bubbling dry hydrogen chloride through the melt for an hour. The hydrogen chloride was generated by dropping concentrated sulfuric acid on pure concentrated hydrochloric acid, and was dried by bubbling through a glass-bead tower containing concentrated sulfuric acid. Silver chloride was prepared by precipitation from a solution of silver nitrate by hydrochloric acid. It was washed repeatedly by decantation with dilute hydrochloric acid solution until freed from nitric acid, and then dried and fused in the absence of light. Small sticks were prepared by pouring the fused silver chloride into graphite molds. Sodium chloride of the highest purity from commercial sources was freed from moisture by drying in an electric oven at 300° for two hours.

The cell containers were made of Pyrex glass tubing in a simple U-tube form, 1 cm. in diameter and 20 cm. long, as shown in Fig. 1. C, in the figure, represents two copper wires, one of which is soldered by means of german silver to a tungsten wire, D, and the other to a silver wire, A. B is a solid solution of silver and sodium chlorides; F is solid lead chloride; and E is solid lead.

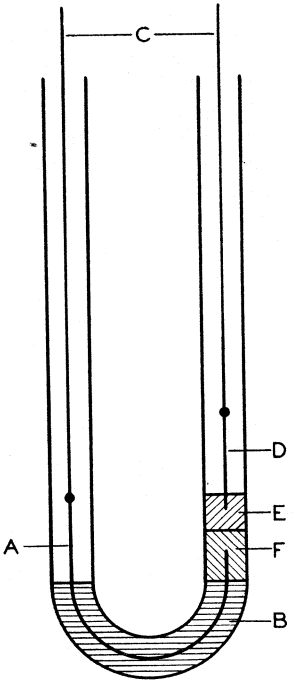

Fig. 1.—Cell container.

The hand-regulated, high temperature thermostat consisted of a well insulated three-liter beaker filled with a good grade of heavy motor oil which was electrically heated and efficiently stirred.

The thermometers employed in measuring the temperature of the bath were compared with primary standards which had been certified by the Bureau of Standards and which were used for standardization purposes only. The accuracy was about 0.1°.

An electrical, hand-regulated crucible furnace with a chamber 7 × 15 cm. was employed for annealing purposes. Its temperature was measured by a chromel–alumel thermocouple connected to a potentiometer indicator.

All electromotive force measurements of the cells were made on a Leeds and North-

[10] Zhemchuzhnui, *Z. anorg. allgem. Chem.*, **153,** 47 (1926).

[11] Tubandt and Eggert, *ibid.*, **110,** 196 (1920).

[12] Treis, *Neues Jahr. Mineral. Geol., Beilage Band,* **37,** 766 (1914).

[13] Lewis and von Ende, THIS JOURNAL, **32,** 732 (1910).

rup type K potentiometer in conjunction with a high resistance galvanometer with a sensitivity of 2075 megs. Special care was taken to insulate all lead wires and mercury cups were used wherever possible to make electrical contact. Since the resistance of the cells in the thermostat varied from about 50,000 to 100,000 ohms, it was easily possible to read their e. m. f. to 0.1 mv.

**Experimental Procedure.**—The silver electrode was inserted around the bend in the empty glass cell. Weighed quantities of silver and sodium chlorides were then dropped into the other arm, fused in the blast lamp and permitted to solidify. Care must be taken to have the tip of the silver wire project about 1 cm. out of the melt. The cell was then placed in the annealing furnace, where it was kept at a temperature just below the melting point of the solid solution for about twenty-four hours. During the last few hours of this period the temperature was slowly lowered until room temperature was reached. Lead chloride was fused and poured into the open arm of the cell, covering the projecting tip of the silver wire. Lead was then melted into the cell, covering the solid lead chloride, and the tungsten–copper wire inserted. The cell was immediately put into the oil-bath. Both the silver and tungsten wires were kept below the surface of the bath to avoid any possible thermocouple potentials. Equilibrium was established within twenty-four hours at 200°. The composition of the solid solutions was varied from mole fraction 1 to 0.160 of silver chloride. The temperature of the bath covered the range 200 to 300° for the cells containing pure silver chloride and 150 to 230° for those containing the solid solutions. It was never permitted to change at a rate greater than about 5° an hour, so that a simultaneous reading of the e. m. f. and temperature proved quite satisfactory. Readings were taken over a period of one or two weeks, all of the cells being constant to within 0.5 mv.

The high temperatures at which the cells were kept, the care taken to avoid rapid fluctuations of temperature, the rapidity with which the cells responded to changes of temperature, the reproducibility of the results with different cells ascending and descending the temperature scale, as well as the constancy of any cell after several weeks in the high temperature bath, indicate a well-defined, reversible reaction reasonably free from disturbing factors.

Several cells were constructed of the form $Pb/PbCl_2/AgCl/Ag$, where the silver wire was not in contact with the lead chloride. With none of these cells could reproducible results be obtained. Obviously, we are dealing here with a variable potential across the interface between silver chloride and lead chloride.

## Experimental Results

The results of the e. m. f. measurements are given in Table I and plotted for two compositions in Fig. 2. The values for pure silver chloride represent four different cells, indicated in the figure by points of different styles. The agreement, it is observed, is quite good. The average deviation of the points from the straight line of the plot is less than 0.5 mv. The e. m. f. of the cell containing pure silver chloride extrapolated to 25° is 0.4879 v. as compared with 0.4883 v. from the "International Critical Tables,"[14] a difference of only 0.4 mv.

Since the variation of e. m. f. with composition is of greatest interest to us, a large-scale plot of Fig. 2 was made and the values of the e. m. f. for the different compositions read off at 150 and 200°. This is given in Fig. 3. Using the relation $\Delta F = -23{,}074\ \mathbf{NE}$, where **N** is the number

[14] "International Critical Tables," 1930, Vol. VII, pp. 248, 265.

TABLE I

E. M. F. IN VOLTS OF CELLS CONTAINING SILVER CHLORIDE OF VARIOUS MOLE FRACTIONS, $N_1$, DILUTED WITH SODIUM CHLORIDE

| $t$, °C. | E. m. f. |
|---|---|
| $N_1$ = 1.000 | |
| 201.5 | 0.4568 |
| 203.7 | .4564 |
| 208.5 | .4549 |
| 210.5 | .4548 |
| 213.6 | .4539 |
| 218.0 | .4526 |
| 223.0 | .4512 |
| 225.3 | .4512 |
| 232.3 | .4487 |
| 234.1 | .4486 |
| 238.9 | .4474 |
| 243.2 | .4468 |
| 245.9 | .4462 |
| 250.4 | .4454 |
| 253.7 | .4446 |
| 261.6 | .4424 |
| 269.9 | .4408 |
| 272.6 | .4400 |
| 279.5 | .4383 |
| 284.6 | .4373 |
| 287.7 | .4366 |
| 289.3 | .4357 |
| 295.4 | .4350 |
| 298.5 | .4341 |
| $N_1$ = 0.870 | |
| 149.7 | .4618 |
| 155.8 | .4605 |
| 159.8 | .4593 |
| 174.5 | .4561 |
| 189.2 | .4535 |
| 191.3 | .4530 |
| 195.2 | .4519 |
| 196.2 | .4523 |
| 206.4 | .4502 |
| 208.9 | .4496 |
| 211.7 | .4490 |
| 217.8 | .4470 |
| 221.3 | .4469 |
| $N_1$ = 0.805 | |
| 171.3 | 0.4571 |
| 172.6 | .4568 |
| 174.3 | .4565 |
| 176.3 | .4560 |
| 182.2 | .4548 |
| 192.3 | .4527 |
| 214.0 | .4482 |
| $N_1$ = 0.719 | |
| 150.4 | .4619 |
| 153.0 | .4611 |
| 156.0 | .4604 |
| 159.8 | .4596 |
| 167.2 | .4580 |
| 172.2 | .4568 |
| 175.2 | .4564 |
| 178.8 | .4556 |
| 187.7 | .4535 |
| 190.5 | .4530 |
| 196.5 | .4518 |
| 206.5 | .4499 |
| 208.8 | .4494 |
| 211.7 | .4487 |
| 221.3 | .4467 |
| $N_1$ = 0.636 | |
| 165.4 | .4571 |
| 168.5 | .4559 |
| 175.7 | .4543 |
| 177.5 | .4542 |
| 180.3 | .4533 |
| 181.1 | .4529 |
| 196.5 | .4498 |
| 203.8 | .4483 |
| $N_1$ = 0.601 | |
| 172.4 | .4561 |
| 178.7 | .4554 |
| 183.6 | .4538 |
| 188.7 | .4526 |
| 192.1 | 0.4519 |
| 200.4 | .4497 |
| 204.8 | .4489 |
| 212.3 | .4471 |
| 216.0 | .4462 |
| 223.7 | .4444 |
| $N_1$ = 0.596 | |
| 172.4 | .4561 |
| 179.6 | .4543 |
| 183.6 | .4532 |
| 188.7 | .4523 |
| 192.1 | .4513 |
| 199.5 | .4494 |
| 200.6 | .4492 |
| 204.9 | .4486 |
| 212.3 | .4468 |
| 216.1 | .4461 |
| 223.7 | .4446 |
| $N_1$ = 0.440 | |
| 168.3 | .4566 |
| 172.4 | .4558 |
| 179.0 | .4542 |
| 192.0 | .4519 |
| 192.5 | .4510 |
| 199.2 | .4490 |
| 200.4 | .4503 |
| 204.3 | .4481 |
| 209.9 | .4472 |
| 210.7 | .4465 |
| 212.7 | .4464 |
| 215.3 | .4460 |
| $N_1$ = 0.368 | |
| 177.1 | .4552 |
| 180.1 | .4546 |
| 187.7 | .4527 |
| 193.5 | .4515 |
| 195.4 | .4509 |
| 196.6 | .4506 |
| 199.9 | .4498 |
| 210.0 | 0.4476 |
| $N_1$ = 0.296 | |
| 152.7 | .4610 |
| 155.5 | .4603 |
| 158.2 | .4597 |
| 164.2 | .4589 |
| 166.8 | .4578 |
| 174.7 | .4562 |
| 178.2 | .4555 |
| 183.6 | .4539 |
| 188.7 | .4534 |
| 192.1 | .4524 |
| 198.2 | .4508 |
| 202.0 | .4500 |
| 204.9 | .4495 |
| 208.0 | .4489 |
| 212.3 | .4478 |
| 216.1 | .4469 |
| 224.6 | .4452 |
| $N_1$ = 0.193 | |
| 149.5 | .4612 |
| 152.6 | .4606 |
| 155.9 | .4596 |
| 189.1 | .4520 |
| 189.7 | .4513 |
| 218.2 | .4440 |
| $N_1$ = 0.160 | |
| 170.8 | .4555 |
| 184.4 | .4519 |
| 187.7 | .4512 |
| 190.7 | .4504 |
| 196.4 | .4490 |
| 197.6 | .4486 |
| 200.7 | .4478 |
| 206.3 | .4463 |
| 209.0 | .4456 |
| 211.7 | .4449 |
| 221.4 | .4427 |

of equivalents per mole, and **E** is the e. m. f. in volts, we calculate $\Delta F$, the free energy of the cell reaction. This varies with the mole fraction of silver chloride, $N_1$, and we will use $\Delta F^\circ$ to denote pure silver chloride. The partial molal free energy of silver chloride in solution, $\bar{F}_1$, is then $\bar{F}_1 = \Delta F^\circ - \Delta F$. The entropy change for the cell reaction, $\Delta S$, is given

in calories per mole per degree by $\Delta s = 23{,}074\ \mathbf{N}\ d\mathbf{E}/dT$, and the partial molal entropy $\bar{s}_1 = \Delta s^\circ - \Delta s$. The change in heat content is $\Delta H = \Delta F - T\Delta S$ and the partial molal heat $\bar{H}_1 = \Delta H^\circ - \Delta H$. The activity of silver chloride in its solutions, $a_1$, taking pure silver chloride as the standard state, is calculated by the relation $\bar{F}_1 = RT \ln a_1$. The activity of the sodium chloride, $a_2$, is obtained by means of the Duhem equation in the integrated form

$$\log \frac{a_2}{N_2} = \int_1^{N_2} \frac{N_1}{N_2}\, d \log \frac{a_1}{N_1}$$

performing a graphical integration and taking pure sodium chloride as the standard state. The thermodynamic values so calculated are given in Table II and the activity at 150° is plotted in Fig. 4. The straight diagonal lines represent Raoult's law.

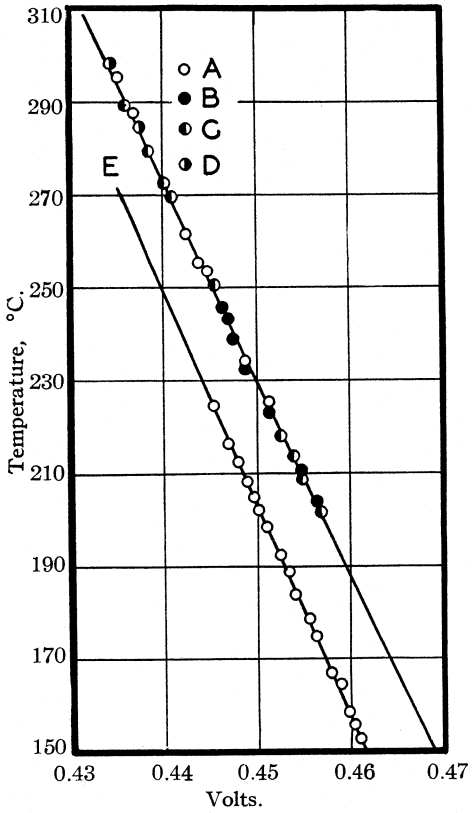


Fig. 2.—Temperature variation of e. m. f. of cells containing two different mole fractions of silver chloride–sodium chloride solutions. Mole fraction of silver chloride in A, B, C and D is 1.000, and in E is 0.296.

## Discussion of Results

In most liquid systems it is possible to produce a slight degree of supersaturation. In no case has an investigation been made of a system going through a complete course of supersaturation wherein it passes continuously from the composition stable at the normal breakdown temperature to another composition also stable at that temperature. The smaller the mobilities of the solute molecules the greater the degree of supersaturation it is possible to attain. It is entirely conceivable that in solid solutions, where the ions possess relatively small mobilities, an unstable, supersaturated condition might persist indefinitely. Inspection of the activity curves in Fig. 4 shows that we are dealing here with a unique system in which, over a range of compositions, the activity of either constituent decreases while its mole fraction increases. A continuous, complete curve of supersaturation is experimentally obtained.

TABLE II

THERMODYNAMIC PROPERTIES OF SILVER CHLORIDE DILUTED WITH SODIUM CHLORIDE

| $N_1$ | $dE/dT$, mv./deg. | $-\Delta S$, cal./deg. | $\bar{S}_1$, cal./deg. | $-\Delta H$, cal. | $-\bar{H}_1$, cal. |
|---|---|---|---|---|---|
| 1.000 | 2.32 | 10.71 | 0 | 26150 | 0 |
| 0.900 | 2.14 | 9.88 | −0.83 | 25560 | 590 |
| .800 | 2.12 | 9.78 | − .93 | 25440 | 710 |
| .700 | 2.16 | 9.97 | − .74 | 25490 | 660 |
| .600 | 2.22 | 10.25 | − .46 | 25580 | 570 |
| .500 | 2.24 | 10.34 | − .37 | 25620 | 530 |
| .400 | 2.26 | 10.43 | − .27 | 25690 | 460 |
| .300 | 2.24 | 10.34 | − .37 | 25680 | 470 |
| .200 | 2.40 | 11.08 | + .37 | 25980 | 170 |
| .100 | 2.70 | 12.46 | +1.75 | 26400 | −250 |

150°

| $N_1$ | E, volts | $-\Delta F$, cal. | $-\bar{F}_1$, cal. | $a_1$ | $a_2$ |
|---|---|---|---|---|---|
| 1.000 | 0.4685 | 21620 | 0 | 1 | 0 |
| 0.900 | .4632 | 21380 | 240 | 0.748 | 0.155 |
| .800 | .4615 | 21300 | 320 | .681 | .354 |
| 700 | .4608 | 21270 | 350 | .655 | .711 |
| .600 | .4605 | 21250 | 370 | .645 | .962 |
| .500 | .4605 | 21250 | 370 | .645 | .955 |
| .400 | .4610 | 21280 | 340 | .663 | .930 |
| .300 | .4617 | 21310 | 310 | .689 | .908 |
| .200 | .4613 | 21290 | 330 | .674 | .910 |
| .100 | .4578 | 21130 | 490 | .556 | .935 |

200°

| | | | | | |
|---|---|---|---|---|---|
| 1.000 | .4569 | 21090 | 0 | 1 | |
| 0.900 | .4525 | 20880 | 210 | 0.806 | |
| .800 | .4509 | 20810 | 280 | .745 | |
| .700 | .4500 | 20770 | 320 | .713 | |
| .600 | .4494 | 20740 | 350 | .692 | |
| .500 | .4493 | 20730 | 360 | .689 | |
| .400 | .4497 | 20750 | 340 | .702 | |
| .300 | .4505 | 20790 | 300 | .731 | |
| .200 | .4493 | 20730 | 360 | .689 | |
| .100 | .4443 | 20510 | 580 | .539 | |

Tammann and his co-workers,[15] investigating the chemical properties of a large number of solid solutions, have discovered striking discontinuities in the variations of the intensity of action with the concentration of the solid solution. This phenomenon he has labeled "limits of resistance." For silver chloride–sodium chloride solid solutions which were extracted with water it was found that crystals with less than five-eighths mole of silver chloride yield all their sodium chloride, while those with more than six-eighths mole lose none of it. In the range of five-eighths to six-eighths,

[15] Tammann, *Z. anorg. allgem. Chem.*, **107**, 1 (1919); Schmidt, Dissertation, Göttingen, 1917.

rapidly increasing amounts were extracted. On the basis of numerous such experiments and because the resistance limits for cubic crystals

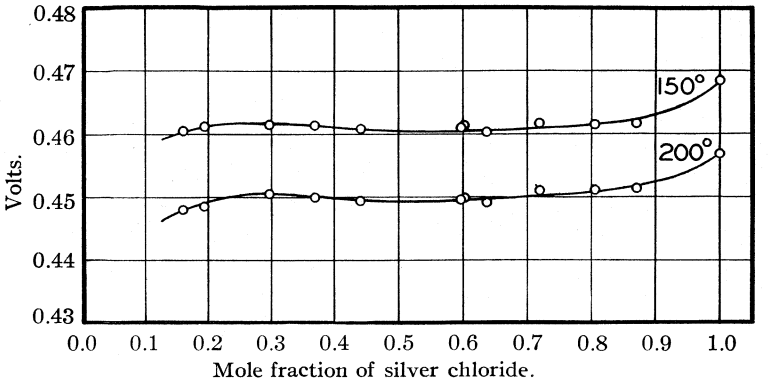


Fig. 3.—Variation of e. m. f. of cells with composition.

can be expressed as multiples of one-eighth mole of one of the two constituents, Tammann draws his fundamental conclusion that the arrange-

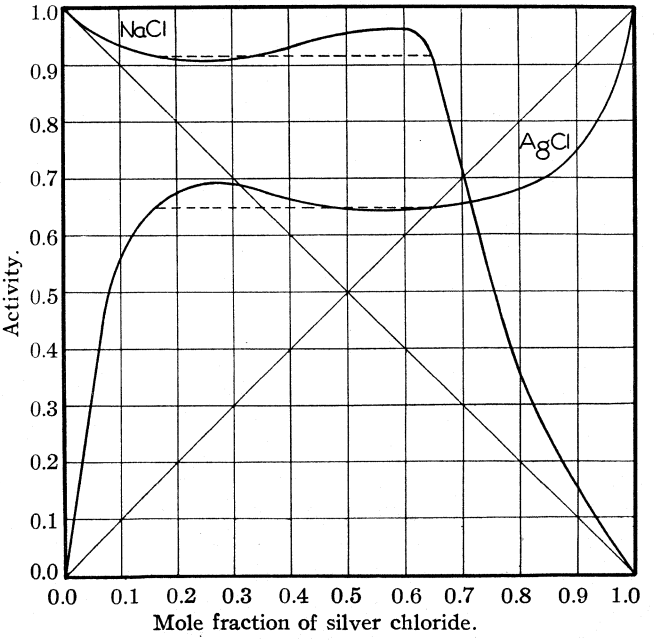


Fig. 4.—Activity curves for silver chloride–sodium chloride solid solutions at 150°.

ment of foreign atoms in solid solutions is regular. A regular arrangement in the silver chloride–sodium chloride solid solutions would consist

of the substitution of eight sodium ions for the silver ions at the corners of the silver chloride unit cell. This, in effect, can be regarded as a loose compound.

The opposing view is taken by Vegard,[16] who, from many x-ray investigations of the changes in lattice constant of solid solutions with composition, concludes that substitution is perfectly random, because a regularity in substitution would give rise to new interference maxima and none have ever been observed.[17] At best, however, these new lines would be very weak.

Experimental determinations of the deviations from Raoult's law for each component of a binary solution furnish a sensitive means of determining the nature of the solution. Increasing positive deviations[18] indicate an increasing tendency toward unmixing and the formation of two phases. Increasing negative deviations indicate the possibility of compound formation, since such a factor would reduce the activities of both components and would tend to annul the effect of any factor which produces abnormally large activities. An examination of Fig. 4 yields the information, then, that as sodium chloride is added to silver chloride, there is, at first, a tendency toward formation of a partly dissociated compound. As the proportion of sodium chloride increases, a very strong tendency toward unmixing manifests itself. However, the solution does not break down into two phases. The supersaturated condition persists through a minimum point of inflection and a maximum of the activity curve until the stable, homogeneous phase rich in sodium chloride is reached. A considerable portion of the sodium chloride activity curve lies above the value 0.9, indicating an extremely large escaping tendency from solution. Abruptly, at mole fraction 0.625 of silver chloride, this curve drops extremely rapidly, compound formation enormously reducing the escaping tendency of the sodium chloride. This completely confirms the extraction results of Tammann. However, the indications are that the "normal" distribution is not the only factor operating in this system to produce "limits of resistance," but that a very strong tendency toward separation into two phases intensifies this phenomenon.

Broomé[17] found that an x-ray analysis of a solid solution containing four-eighths mole of silver chloride showed two patterns indicating unmixing at room temperature. LeBlanc and Quenstadt,[19] however, found no unmixing after keeping the crystals for six weeks at room temperature.

The broken lines in Fig. 4 were obtained graphically by drawing two

[16] Vegard, *Z. Physik*, **5**, 17 (1921).

[17] Broomé, *Z. anorg. allgem. Chem.*, **143**, 60 (1925).

[18] *Cf.* Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924, pp. 55, 72.

[19] LeBlanc and Quenstadt, *Z. physik. Chem.*, [Abt. A] **150**, 321 (1930).

horizontal lines so that each one would intersect the stable portion of its respective activity curve at the same mole fraction. The values of the mole fraction, $N_1$, thus obtained are 0.835 and 0.352. These values represent the compositions at which unmixing should occur. Inspection of these curves shows that only one pair of horizontal lines will satisfy the above conditions.

Experiments are now in progress applying these methods to other solid solutions. It is hoped that extending the temperature range, especially in the direction of lower temperatures, will yield a more thorough knowledge of the nature of these solutions. Certainly, we would expect to find that any tendency toward the formation of compounds would become intensified with a decrease in temperature.

## Summary

1. The technique of making precise potential measurements of galvanic cells containing solid electrolytes has been described.

2. The energy changes of solid silver chloride upon a dilution with sodium chloride have been determined at mole fractions of silver chloride varying from 1 to 0.160, between the temperatures of 150 and 230°.

3. The course of an activity curve for a supersaturated condition has been followed experimentally over its complete range of composition.

4. It is pointed out that Tammann's "limits of resistance" can be explained on the basis of this type of activity function.

5. The existence of a regular arrangement of sodium ions in the silver chloride–sodium chloride lattice is verified.

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE LABORATORIES OF THE COLUMBIA CHEMICAL DIVISION OF THE PITTSBURGH PLATE GLASS CO., AND OF NEW YORK UNIVERSITY]

# AQUEOUS SOLUBILITY OF SALTS AT HIGH TEMPERATURES. I. SOLUBILITY OF SODIUM CARBONATE FROM 50 TO 348°[1]

BY WILLIAM F. WALDECK, GEORGE LYNN AND ARTHUR E. HILL

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This investigation was carried out for the purpose of developing a satisfactory method for the determination of solubilities at high temperatures and pressures, and with its aid determining the solubility of sodium carbonate up to the critical temperature of water. From the solubility curve it was intended to ascertain the temperature of the transition of the monohydrate to the anhydrous form in contact with the solution under its own vapor pressure.

**Previous High-Temperature High-Pressure Solubility Methods.**—The

[1] Presented by W. F. Waldeck as thesis for the degree of Master of Science at New York University.

sealed tube or plethostatic method,[2] which consists in noting the temperature at which the last trace of solid in a synthetic mixture disappears, is the oldest and still the most common method. It apparently was first used by Guthrie[3] for potassium nitrate in water at high temperatures. It was later applied by Alexejew[4] to the determination of the mutual solubility of liquids. Wuite's[5] classical work on sodium sulfate up to the critical temperature of water was carried out with the sealed tube method, using tubes of quartz at the higher temperatures. The exhaustive work of Morey[6] on the ternary system $H_2O$–$K_2SiO_3$–$SiO_2$, going up to temperatures of 1000° and pressures of 560 atmospheres, was accomplished by a "hydrothermal quenching method," which was in effect a plethostatic one.

Direct solubility measurements by withdrawal or isolation of a sample of the saturated solution at high temperatures seem to have been first accomplished by Tilden and Shenstone,[7] who used a silver-plated steel tube divided into two compartments by a platinum gauze, equilibrium being attained in the one compartment and a sample filtered into the other by simply inverting the tube. Upon cooling, the total sample was analyzed. The values they obtained, together with those of Étard,[8] who used a similar apparatus of glass for a great many salts, have been shown to be of doubtful accuracy by more recent work.

Partridge,[9] Boyer-Guillon[10] and Hall, Robb and Coleman,[11] have measured the solubility of calcium sulfate in water at elevated temperatures by withdrawing large quantities of solution from directly heated autoclaves.

Seyer and Todd[12] have utilized a small solubility device made of pipe fittings so arranged that tilting the tube would cause part of the solution to flow into a weighed sidearm. On cooling, the contents of the sidearm were analyzed.

The best of these direct solubility devices was that used by Robson[13] for magnesium sulfate. This was a small gold-lined monel metal bomb with a valve to permit withdrawal of a sample into a weighed, water-cooled copper tube, the sample being filtered through an alundum disk. Failure of the gold gasket above 240° and crystallization in the valve limited the

[2] For the terminology of solubility methods see Hill, THIS JOURNAL, **45**, 1143 (1923).

[3] Guthrie, *Phil. Mag.*, **18**, 105 (1884).

[4] Alexejew, *Ann. Physik*, **28**, 305 (1886).

[5] Wuite, *Z. physik. Chem.*, **46**, 818 (1903).

[6] Morey, THIS JOURNAL, **39**, 1173 (1917).

[7] Tilden and Shenstone, *Phil. Trans. Roy. Soc.* (London), **175**, Pt. 1, 23 (1884).

[8] Étard, *Ann. chim. phys.*, [7] **2**, 503 (1894).

[9] Partridge, THIS JOURNAL, **51**, 360 (1929).

[10] Boyer-Guillon, *Ann. Conservatoire Arts et Metiers*, [3] **2**, 207 (1900).

[11] Hall, Robb and Coleman, THIS JOURNAL, **48**, 927 (1926).

[12] Seyer and Todd, *Trans. Roy. Soc. Can.*, [3] **23**, 67 (1929).

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

usefulness of the device and made a contemplated ternary investigation impossible.

The solubility of some sparingly soluble salts has been determined indirectly by conductance measurements in a Noyes and Coolidge[14] bomb by Melcher.[15]

Apparatus for the investigation of pressure on solubilities at room temperature has been developed by von Stackelberg,[16] by Cohen and Sinnige[17] and by others.

Though some notably accurate solubility work[18] has been done with the sealed tube method, the inability of glass or quartz tubes to withstand the high pressures, the severe etching on the glass, and the impossibility of securing direct pressure measurements all made a direct measurement in bombs seem desirable.

**Previous Solubility Values for Sodium Carbonates.**—The most careful measurements of the aqueous solubility of sodium carbonate are those of Wells and McAdam[19] from 27.84 to 43.94°. Above this temperature the determinations are surprisingly few, and are due only to Mulder,[20] to Epple and to Seyer and Todd, the latter being the only work above the normal boiling point of the saturated solution. The values of Mulder and of Epple agree well with each other and apparently are the basis of the "International Critical Table" values. Seyer and Todd give values much below those of Mulder and Epple, and find at 149° a break in the solubility curve which they attribute to the transition of the monohydrate to the anhydrous form.

Jänecke[21] has given 107° as the transition of the monohydrate to the anhydrous forms, having obtained this value by applying pressure to dry, solid monohydrate, increasing the temperature and noting the temperature at which the sudden drop in pressure indicated that there had formed anhydrous crystals, and solution which escaped through small holes into another compartment. Due to the fact that the pressure applied to the monohydrate was in the neighborhood of 455 atmospheres, the value of 107° is probably widely different from the value at the pressures of the saturated solution.

[14] Noyes and Coolidge, *Publ. Carnegie Inst., Washington*, **63**, 59 (1907).

[15] Melcher, THIS JOURNAL, **32**, 50 (1910).

[16] Von Stackelberg, *Z. physik. Chem.*, **20**, 337 (1896).

[17] Cohen and Sinnige, *Trans. Faraday Soc.*, **5**, 269 (1905).

[18] Kracek, *J. Phys. Chem.*, **35**, 417, 947 (1931); Kracek, THIS JOURNAL, **53**, 2620 (1931).

[19] Wells and McAdam, *ibid.*, **29**, 726 (1907).

[20] Mulder, "Scheikundige Verhandelingen en Onderzoekingen," Vol. 3, Pt. 2, "Bijdragen tot de Geschiedenis van Het Scherkungig Gebonden Water," Rotterdam, 1864, as quoted in Seidell, "Solubilities of Inorganic and Organic Compounds," 2d ed.; Epple, Dissertation, Heidelberg, 1899, as quoted in Landolt-Börnstein, "Tabellen."

[21] Jänecke, *Z. physik. Chem.*, **90**, 269 (1915).

## Experimental Work

**Apparatus and Method.**—Most of the solubility determinations were made in the Type I bomb shown in section in Fig. 1. It was made entirely of Allegheny Metal (18% Cr, 8% Ni steel) and was fitted with a sampler, a relief valve and a capillary tube leading to a pressure gage. A copper gasket was used on the main joint. Considerable difficulty was experienced in keeping the sampler-valve stem tight until the "oxygen-tank" type of valve, as shown, was tried. A rubber disk, stock no. 76-S Soft Superbo Bibb Washer, Woodward Wanger Company, served satisfactorily as a valve disk up to 350°. In this type of valve, both the internal pressure and the external spring force the shoulder on the valve stem against the valve disk, thus sealing the device. The valve disk must therefore be hard enough under conditions of high temperature and pressure to withstand being forced out of the valve by the high pressure, but must also be soft enough at low temperatures, with the sampler evacuated, to seal effectively with only the tension of the spring holding the shoulder against the disk.

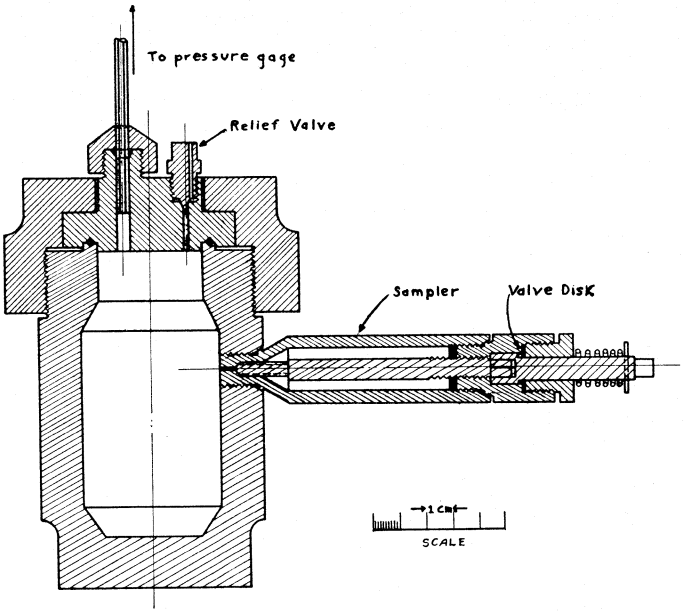


Fig. 1.—Type I solubility bomb.

The bomb was mounted in an oscillating cradle with the sampler valve-stem on the axis of oscillation and extending outside the electrically heated air-bath. This air-bath, of about 60 × 30 × 40 cm. dimensions, was made of asbestos cement board and insulated with 2.5 cm. of Sil-O-Cel. The heating coils were mounted in a box of asbestos board with both ends open, this forming a wind tunnel, supported inside the air-bath. A fan circulated the air through this wind tunnel and over the coils. Temperature regulation to about ±1° was obtained by use of a de Khotinsky bimetallic-strip thermoregulator specially soldered to withstand 400°. Temperatures were read from a calibrated thermometer with its bulb in the air stream. The bomb was oscillated fourteen times per minute through an arc of 115° from the vertical.

Due principally to heat losses through the sampler and cradle shaft, the temperature within the bomb was lower than that in the air-bath. This difference was compensated

for from a temperature correction curve prepared by inserting a thermo-element in a suitable non-volatile liquid in the bomb and taking simultaneous bomb and air-bath temperatures. The thermo-element was suitably calibrated, and sufficient time was allowed for the bomb to come to thermal equilibrium, two hours usually sufficing. This temperature correction varied from 2 at 100° to 23 at 400°.

In making a solubility determination, the sampler, which weighed about 450 g., was assembled, evacuated, weighed and screwed into the bomb. To the bomb were then added sufficient water, and reagent quality sodium carbonate in excess, to establish the liquid level well above the sampler orifice. Care was taken to allow sufficient space for thermal expansion so as not to fill the bomb completely and thus create enormous pressures. After the bomb was closed securely and placed in position in the cradle, the temperature of the air-bath was raised to about 25° above the desired temperature for an hour and then dropped back to the steady value for from four to eight hours. A series of solubility tests at 100° of varying duration showed saturation to be attained in less than four hours.

Oscillation was stopped and the bomb allowed to stand for thirty minutes in a vertical position before the sampler valve was opened. After one minute the valve was closed and the air-bath opened to cool. When cold, the sampler was unscrewed from the bomb, washed externally with water, dried and weighed to the nearest 10 mg., thus giving the weight of the sample (usually about 10 g.) to one part in a thousand. The sampler was then opened and the contents carefully washed into an Erlenmeyer flask with hot distilled water. The sodium carbonate was determined by titration with 1 *N* hydrochloric acid using methyl orange as indicator, and boiling out the carbon dioxide before the end-point was reached.

A check on the accuracy of the method was made by determining the solubility from 50 to 100° in a glass apparatus as used by Simmons and Waldeck[22] on lithium bromate. Here equilibrium was approached from both supersaturation and undersaturation. These values agreed well with those obtained with the bomb at 100°, the lowest temperature reached with the bomb. A further check was obtained at higher temperatures using an improved type of bomb with the sampler inside the bomb. In this case no temperature correction was made as the bomb was wholly within the air-bath. This new bomb will be described in a later paper.

**Corrosion.**—After the first few runs in the bombs, the inside surfaces became covered with a hard, black, adherent coating. This could not be removed by pickling, was taken off only with difficulty by emery, and was therefore left on. There was no noticeable contamination of the residual solution until temperatures of 200° and above were reached, when a slight yellow coloration was apparent. Above 300° the solution became strongly yellow colored, although curiously enough a solution that was heated to the critical temperature showed no coloration.

The most highly colored solution showed 0.0005% Fe, which was certainly as low as the original sodium carbonate, and negligible in any case. Treatment with dimethylglyoxime gave a barely visible cloudiness, and in view of the voluminous nature of this precipitate, this was taken as evidence of an extremely low nickel content. The color was undoubtedly due to chromium, since analysis showed 0.006% Cr. A solution of sodium chromate of the same chromium content showed an identical color.

[22] Simmons and Waldeck, THIS JOURNAL, **53**, 1725 (1931).

**Accuracy.**—The results, represented by Table I and the curve shown in Fig. 2, are believed to be accurate to within 0.1% sodium carbonate, from

TABLE I

SOLUBILITY OF SODIUM CARBONATE

| Temp., °C. | $Na_2CO_3$, % | Apparatus | Temp., °C. | $Na_2CO_3$, % | Apparatus |
|---|---|---|---|---|---|
| 50.0 | 32.0 | Glass | 139.0 | 28.1 | Bomb I |
| 60.0 | 31.6 | Glass | 145.0 | 27.7 | Bomb I |
| 75.5 | 31.0 | Glass | 152.0 | 27.7 | Bomb II |
| 83.6 | 30.8 | Glass | 159.0 | 26.8 | Bomb II |
| 99.5 | 30.6 | Bomb I | 170.0 | 26.1 | Bomb II |
| 100.0 | 30.8 | Glass | 174.0 | 25.5 | Bomb I |
| 100.0 | 30.9 | Bomb II | 176.0 | 25.5 | Bomb II |
| 100.5 | 30.8 | Glass | 180.0 | 25.0 | Bomb II |
| 100.5 | 30.8 | Glass | 200.0 | 23.3 | Bomb I |
| 103.0 | 30.8 | Bomb I | 225.0 | 20.7 | Bomb I |
| 106.0 | 30.7 | Bomb I | 239.0 | 18.7 | Bomb I |
| 112.5 | 30.8 | Bomb I | 275.0 | 13.2 | Bomb I |
| 113.0 | 30.8 | Bomb I | 300.0 | 8.4 | Bomb I |
| 116.0 | 30.3 | Bomb I | 301.0 | 8.4 | Bomb I |
| 121.5 | 29.8 | Bomb I | 321.0 | 4.8 | Bomb I |
| 125.0 | 29.5 | Bomb I | 326.0 | 4.4 | Bomb I |
| 131.5 | 28.8 | Bomb I | 348.0 | 0.0 | Bomb I |

50 to 150°, 0.2% from 150 to 250° and 0.3% above 250°. This uncertainty is due to the difference in temperature between the air-bath and the interior of the bomb, and to the fluctuation of the temperature of the

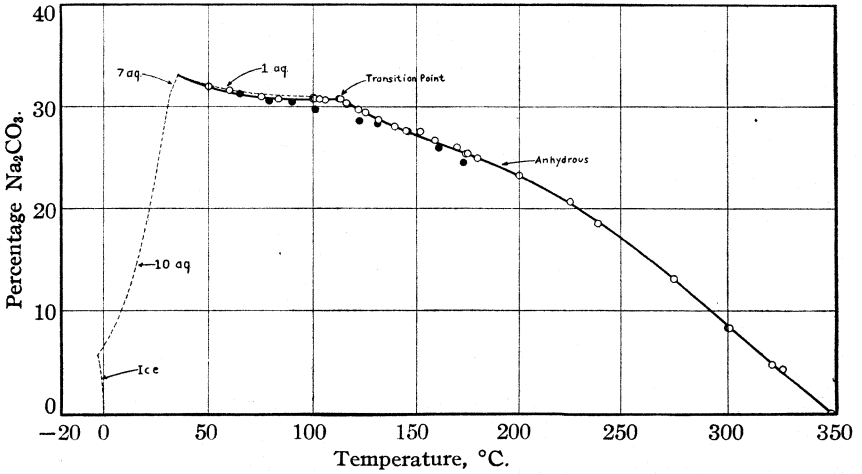


Fig. 2.—The solubility curve of sodium carbonate. – – – "International Critical Tables" values; ●, Seyer and Todd; ○, present work.

air-bath caused by slight sticking of the thermo-regulator contacts. While these rapid fluctuations did not affect the temperature of the bomb appreciably, it made the precise value of the temperature in doubt by about 1°.

**Transition Point.**—It is apparent from the discontinuity of the curve that the transition between the anhydrous and the monohydrated forms occurs at 112.5 ± 1°.

**Anhydrous Crystals.**—Anhydrous crystals were prepared at 140° and at 220° by heating in Bomb I solutions undersaturated at the temperatures in question until thermal equilibrium had been attained. The small valve at the top of the bomb was then opened slightly to permit a slow escape of steam. When no more steam issued from the valve, the bomb was opened while hot and the crystals examined immediately under a petrographic microscope.[23] The crystals tend toward flakes; biaxial, negative; $N_g$ = 1.544, $N_m$ 1.537, $N_p$ 1.410 (±0.001). The two optic axes are inclined in such a way that they are on the same side of the normal to the face of the flake, but one of them very nearly coincides with the normal; measurement with micrometer-eyepiece and Bertrand lens showed: $2E = 43 \pm 2°$, from which $2V = 28 \pm 2°$.

**Vapor Pressure of Saturated Solution.**—Pressure measurements were made by screwing into the socket at the end of the steel capillary, outside the bomb, ordinary Bourdon gages of the most favorable range for each particular measurement. The gages were flushed out with ether to remove oil, dried, and filled with water. They were calibrated on a dead-weight gage tester after each run. The two highest pressures, as recorded in Table II, were measured with a standard test gage. The results are plotted on a Dühring's rule basis[24] in Fig. 3.

TABLE II

THE VAPOR PRESSURE OF SATURATED SOLUTIONS OF SODIUM CARBONATE

| Temp., °C. | Pressure, atmospheres | Temp. at which water has the same pressure | Diff. in temp. between satd. soln. and water at the same pressure |
|---|---|---|---|
| 104.8 | 1.00 | 100.0 | 4.8 |
| 112.0 | 1.27 | 106.9 | 5.1 |
| 121.0 | 1.69 | 115.4 | 4.4 |
| 176.5 | 8.43 | 173.2 | 3.3 |
| 231.0 | 26.6 | 228.0 | 3.0 |
| 313.0 | 99.0 | 310.9 | 2.1 |
| 365.0 | 199 | 366.0 | −1.0 |

The negative value of this difference, at a temperature when the vapor pressure of the solution should be indistinguishable from that of pure water, was undoubtedly caused by the error of reading the gage, which could be read only to the nearest atmosphere, corresponding to 1°.

**Discussion.**—The discrepancy between the other solubility values and ours we do not find explicable. Epple and Mulder give higher values,

[23] The microscopic examination was conducted by Mr. B. K. Beecher.

[24] For a discussion of Dühring's rule see Monrad, *Ind. Eng. Chem.*, **21**, 139 (1929).

although our methods would tend to give high values, due to possible evaporation during sampling with the glass apparatus, or possible inclusion of suspended solid in the sample with the bombs. Epple's values, however, were also found to be high in the lower range of temperature by Wells and McAdam. On the other hand, Seyer and Todd were much more likely to get high values than we, and yet their values are much lower, with a totally different transition temperature.

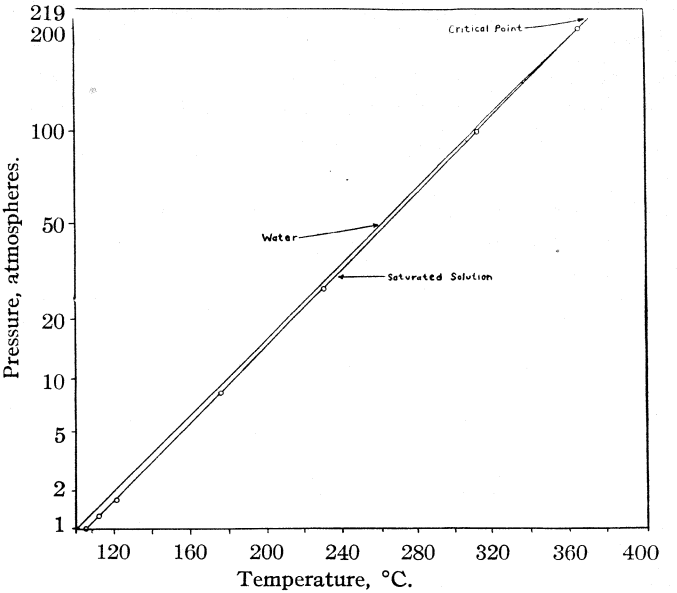


Fig. 3.—The vapor pressure of saturated solutions of sodium carbonate plotted by Dühring's method.

The transition temperature reported by Jänecke is obviously low because of the high pressure of approximately 450 atmospheres prevailing during the determination. Inspection of density values shows that the incongruent melting of monohydrate is attended by a shrinkage in volume, thus explaining the lowering of the transition temperature by pressure.

It is evident that this system is of the second type postulated by Smits,[25] in which the solubility curve intersects the binary critical curve. Since the solubility fell to zero at 348°, within the limits of error of the analysis, no investigations were carried on up to the critical temperature of water, 375°. It is probable that a definite, though undetectable, solubility exists at temperatures higher than 348°.

**Acknowledgment.**—The authors record with gratitude the active aid of the Research Laboratory of the Columbia Chemical Division, Pittsburgh

[25] Smits, *Z. physik. Chem.*, **51**, 194 (1905).

Plate Glass Company, the generosity of Mr. B. K. Beecher of that laboratory in making the petrographic examination, and the fine workmanship of Mr. William Latham, toolmaker of the Columbia plant, on the bombs, which contributed much to their success.

## Summary

1. Apparatus has been developed for the direct determination of solubilities and pressures at high temperatures and pressures.

2. The solubility of sodium carbonate in water has been determined from 50 to 350°.

3. The transition of the monohydrated into the anhydrous form in contact with solution under its own vapor pressure has been shown to occur at 112.5 ± 1° and 1.27 atmospheres pressure.

4. Crystals of anhydrous sodium carbonate have been grown at elevated temperatures and optical data on them are presented.

5. The vapor pressure of saturated solutions of sodium carbonate has been determined.

NEW YORK, N. Y.

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

# A DOUBLE CAPILLARY METHOD FOR THE MEASUREMENT OF INTERFACIAL TENSION

BY G. L. MACK AND F. E. BARTELL

RECEIVED OCTOBER 23, 1931 PUBLISHED MARCH 5, 1932

In connection with some of our recent work we were confronted with the necessity of determining the interfacial tension of water against several different liquids which were expensive and which were difficult to obtain in large quantities in the pure state. It became highly desirable to develop a method which would require but a small amount of organic liquid for each measurement. The drop volume method of Harkins and the various capillary rise methods previously used, all required appreciable quantities of liquid. Sugden had solved a similar problem for surface tension determinations through the use of either a maximum bubble pressure method[1] or a double capillary method.[2] The first method did not, in its present form, appear to be applicable to the measurement of interfacial tensions. A modification of the second did seem promising.

Quite recently a method for the measurement of interfacial tensions of liquid–liquid systems based upon the principle of capillary rise had been developed, and had been quite generally used in this Laboratory.[3] With this apparatus from 10 to 20 cc. of organic liquid was required for

[1] Sugden, *J. Chem. Soc.*, **119**, 1483 (1921).

[2] Sugden, *ibid.*, **121**, 858 (1922); **125**, 27 (1924).

[3] Bartell and Miller, THIS JOURNAL, **50**, 1961 (1928).

each determination. As work progressed certain modifications were made in the method. It was found that by making use of two capillaries of different diameters an apparatus, similar in operation to the one referred to above, could be constructed which would give very good results and which requires not more than about 2 cc. of organic liquid. The apparatus might then quite properly be referred to as a "*micro apparatus*" for the measurement of interfacial tension.

In order to obtain satisfactory interfacial tension measurements for water against organic liquids it is necessary that the capillary tube be coated by a film of water before the organic liquid is admitted. This necessitates somewhat different procedure for different organic liquids, depending upon whether the density of the organic liquid is greater or less than that of water. It was found that one type of construction was more suitable for the heavier-than-water liquids—and another type for the lighter-than-water liquids. Soft glass capillaries were used in the apparatus as the degree of wetting of soft glass by water is higher than that of certain other glasses such as Pyrex. The soft glass is therefore more readily coated with the necessary initial water film.

**Apparatus for Liquids of Density Greater than that of Water.**—The apparatus for liquids of density greater than that of water is shown in Fig. 1. It consists of two soft glass cups, A and B, each 4 cm. in diameter and 10 cm. in height. The cups are sealed directly to capillary tubes with diameters of about 0.25 and 1.0 mm., respectively. These are joined with 5-mm. tubing to which is sealed a center tube, the upper portion of which is of 10 to 15 mm. bore. This tube has a flared rim.

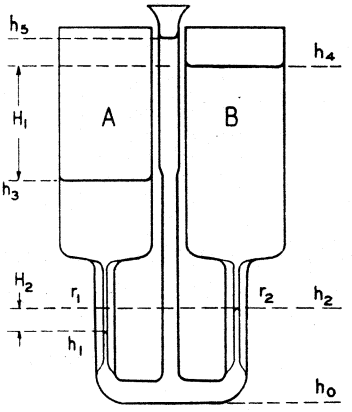

Fig. 1.

In carrying out an interfacial tension determination water is poured into Cup A until both capillaries are filled. No air will be entrapped if the liquid is added through the finer capillary. Ten to fifteen cc. of water is now added to each cup and the three liquid levels allowed to come to equilibrium. Organic liquid is next introduced through the center tube until the two liquid–liquid interfaces reach the lower ends of the capillaries. The organic liquid is then added drop by drop while at the same time water is added to cup B at such a rate as just to prevent the organic liquid from running through the large capillary. When the organic liquid finally enters the lower part of both capillaries the positions of the two menisci are adjusted by suitable addition of liquid so that the smaller meniscus is at a slightly lower level. The organic liquid is now added in small fractions of a drop until the two

menisci rise to the etched reference marks. A total of one or two drops is usually sufficient. Since the head of water over the lower meniscus is the smaller, this meniscus will rise the faster with the result that the final vertical positions of the menisci should be practically identical. The vertical distances, $H_1$ and $H_2$, between the two sets of menisci are now measured with a cathetometer.

As it is practically impossible to get both menisci to coincide exactly with the etch marks the capillaries must be carefully calibrated. Such calibration can be accomplished in the same way as with the original Bartell–Miller apparatus,[3] by employing benzene and water as liquids and accepting the value of 34.72 dynes/cm. as the interfacial tension ($S_{23}$) of this system at 25°. The radius of the capillary at several points at different distances from the reference mark can thus be calculated and a curve plotted from which the radius at any given point can be determined accurately.

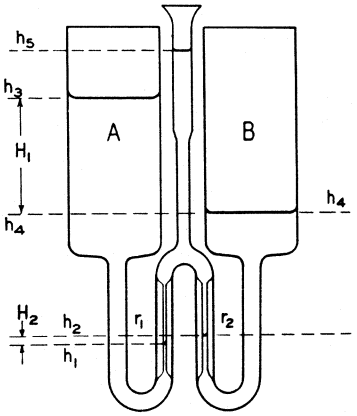

Fig. 2.

**Apparatus for Liquids of Density Less than that of Water.**—The apparatus for the measurement of interfacial tensions of liquids of density less than that of water is shown in Fig. 2. The operation is essentially the same as that described above.

The formulation which can be used for the calculation of interfacial tension by the above methods may be developed as follows.

(*a*) In case $\rho_0$, the density of the organic liquid, is greater than $\rho_w$, the density of water at the same temperature (Fig. 1), the relation between the weight of liquid held in the capillaries and the force holding it at heights $h_1$ or $h_2$, in capillaries of radii $r_1$ and $r_2$, respectively, is given by the expressions

$$2\pi r_1 S_{23} = \pi r_1^2 g\{(h_5 - h_1 + {}^1/_3 r_1)\rho_0 - (h_3 - h_1 + {}^1/_3 r_1)\rho_w\} \quad (1)$$

$$2\pi r_2 S_{23} = \pi r_2^2 g\{(h_5 - h_2 + {}^1/_3 r_2)\rho_0 - (h_4 - h_2 + {}^1/_3 r_2)\rho_w\} \quad (2)$$

Subtracting and simplifying

$$\frac{2S_{23}}{g}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \rho_0\{h_2 - h_1 + {}^1/_3(r_1 - r_2)\} + \rho_w\{(h_4 - h_3) - (h_2 - h_1) + {}^1/_3(r_2 - r_1)\} \quad (3)$$

Putting $H_1 = (h_4 - h_3)$, $H_2 = (h_2 - h_1)$ and $R = (r_2 - r_1)$, we have

$$S_{23} = \frac{g}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)}\{(H_1 - H_2)\rho_w + H_2\rho_0 - {}^1/_3 R(\rho_0 - \rho_w)\} \quad (4)$$

(*b*) In case $\rho_0$ is less than $\rho_w$ (Fig. 2), the formulation is

$$S_{23} = \frac{g}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)}\{(H_1 - H_2)\rho_w + H_2\rho_0 + {}^1/_3 R(\rho_0 - \rho_w)\} \quad (5)$$

The final equations differ only in the sign of the meniscus correction, and since the sign of the quantity $(\rho_0 - \rho_w)$ also changes, equations (4) and (5) can be generalized into

$$S_{23} = \frac{g}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \{(H_1 - H_2)\rho_w + H_2\rho_0 - {}^1/_3 R\Delta\} \qquad (6)$$

where $\Delta$ is the absolute difference between the densities.

It will be noticed that the Poisson equation for capillary rise has been used throughout this work. Rayleigh[4] has pointed out that the equation fails when $r/h$ is much greater than 0.4, the maximum radius of the large capillary is limited to 1 mm.

Sugden[1] has developed for surface tension determinations a method in which any size of capillary may be used. In his table he uses four different equations to cover the entire range of radii values. For interfacial tensions similarly obtained, a table would have to be made up for every range of density differences; accordingly calculations would become very laborious. Richards, Speyers and Carver[5] attempted to use fairly large capillaries. The theoretical basis for their calculations has been attacked by Sugden.[6]

A further advantage of the new type of apparatus, aside from the small amount of liquid used, can be seen from equation (6). If $H_2$ is made very small, the variations in the magnitude of $\rho_0$ will have very little effect on the calculated value of $S_{23}$, and the density of the organic liquid need not be determined more accurately than to two decimal places. This practically disposes of density measurements as a source of error in these interfacial tension determinations.

It is not practical to attempt to make the $H_2$ value exactly zero. A simple modification of the above apparatus can be made, however, which will cause the $H_1$ term to vanish entirely. Equation (6) in this case reduces to

$$S_{23} = \frac{g}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \{H_2(\rho_0 - \rho_w) - {}^1/_3 R\Delta\} \qquad (7)$$

For liquids heavier than water the form of apparatus illustrated in Fig. 3 is used, while that shown in Fig. 4 is used for liquids lighter than water.

Tubing of 5 to 6 mm. bore with flared rims is used for the side arms. The capillaries should have about the same radii as those of the apparatus shown in Figs. 1 and 2. The best relative sizes for the capillaries will vary widely with the density differences of the liquids to be used, the interfacial tension value, and the most desirable length of the apparatus. To facilitate cleaning, the fine capillary is made about 3 cm. in length. The wide capillary should then be about 10 to 20 cm. in length.

The operation of the apparatus is simple. Water is poured into the right arm of the apparatus (Fig. 3 or 4) until the capillaries are filled;

[4] Rayleigh, *Proc. Roy. Soc.* (London), **A92,** 184 (1915).

[5] Richards, Speyers and Carver, THIS JOURNAL, **46,** 1196 (1924).

[6] Sugden, THIS JOURNAL, **47,** 60 (1925).

then the organic liquid is slowly added to the left arm until the meniscus comes just to the etched mark on the fine capillary tube. The vertical distance between the two menisci is then measured with a cathetometer or by means of a graduated scale placed behind the tube (as is indicated in Fig. 3).

The capillaries are calibrated by inverting the apparatus over a comparatively large open vessel of some reference liquid, such as benzene or water. The radii are then calculated from the surface tension formulation. The radius of the small capillary need be known only at the etched mark, but the other capillary must be carefully calibrated throughout its length.

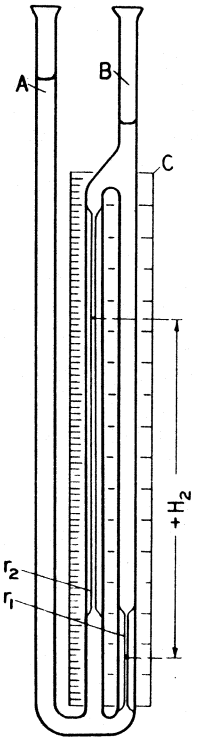

Fig. 3.

These double capillary apparatus (*i. e.*, shown in Figs. 3 and 4) will be best suited to interfacial tension measurements in which very careful density determinations can be carried out. They are obviously not well suited to the measurement of the interfacial tensions of systems which have only a slight density difference, but are best suited to those in which an appreciable difference does exist. In the latter case they have some advantages over the first types shown in Figs. 1 and 2. The determination is more easily carried out, as it is necessary to measure but one height. Only the two capillary menisci are involved, and their positions can be determined with a much greater degree of precision than is possible with a wide meniscus. Indeed, the uncertainty in reading the height of the wide meniscus is one of the objections to the capillary rise methods in general.

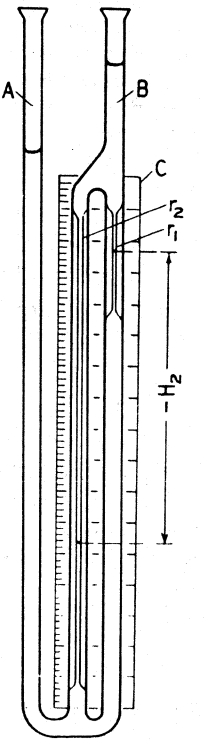

Fig. 4.

It should be noted that the apparatus shown in Fig. 3 is especially adapted to the measurement of the interfacial tensions of mercury against other liquids. Here the density difference would always be large so that an error in determining the density of the lighter liquid would have no magnified effect upon the value, $S_{23}$. The usual methods of measuring the interfacial tension at a water surface cannot be extended with equal success to a mercury surface. The drop weight method has been used with success for this measurement, but it appears to involve serious difficul-

ties in operative technique. The capillary apparatus of Bartell and Miller can be used, but the various capillary rise methods used by Von Lerch,[7] Clark,[8] Harkins and Humphrey[9] and Reynolds[10] cannot be used at all, because the capillary meniscus is below the mercury surface and cannot be seen. Preliminary experiments in this Laboratory indicate that measurements comparing favorably in accuracy with the very care-

TABLE I

INTERFACIAL TENSION DATA

| Organic liquid | Temp., °C. | Density | $H_1$, mm. | $H_2$, mm. | $\frac{1}{r_1} - \frac{1}{r_2}$ | $S_{23}$ dynes/cm. |
|---|---|---|---|---|---|---|
| Apparatus No. 1 | $r_1 = 0.2275 - 0.2300$ mm.[a] $r_2 = 0.5550 - 0.5580$ mm. | | | | | |
| Nitrobenzene | 15.13 | 1.1981 | 13.73 | +1.39 | 2.574 | 26.65[b] |
| Chlorobenzene | 25.13 | 1.1008 | 20.02 | −0.32 | 2.575 | 37.93 |
| Carbon bisulfide | 25.13 | 1.2555 | 26.30 | −3.50 | 2.572 | 48.14 |
| Apparatus No. 2a | $r_1 = 0.1957 - 0.1961$ mm. $r_2 = 0.5209 - 0.5236$ mm. | | | | | |
| Benzene | 25.13 | 0.8734 | 22.34 | −2.68 | 3.194 | 34.71 |
| Toluene | 30.12 | .8563 | 23.34 | −1.63 | 3.188 | 35.90 |
| Ethylbenzene | 25.13 | .8625 | 25.09 | +0.59 | 3.189 | 38.33 |
| Propylbenzene | 25.13 | .8675 | 26.21 | +0.82 | 3.192 | 39.98 |
| Apparatus No. 2b | $r_1 = 0.2310 - 0.2320$ mm. $r_2 = 0.5715 - 0.5731$ mm. | | | | | |
| Benzene | 25.13 | 0.8734 | 18.26 | −0.40 | 2.574 | 34.74 |
| Butylbenzene | 25.13 | .8561 | 21.89 | +0.34 | 2.566 | 41.58 |

[a] The data given for $r_1$ and $r_2$ in these tables represent the limiting values of the radii of the capillaries. [b] The value given for each determination represents the mean of three or more determinations.

TABLE II

INTERFACIAL TENSION DATA

| Organic liquid | Temp., °C. | Dens. diff. | $H_2$, mm. | $\frac{1}{r_1} - \frac{1}{r_2}$ | $S_{23}$ dynes/cm. |
|---|---|---|---|---|---|
| Apparatus No. 3 | $r_1 = 0.2490 - 0.2510$ $r_2 = 0.5600 - 0.5680$ | | | | |
| Benzene | 25.13 | 0.1237 | 127.8 | 2.235 | 34.68 |
| Toluene | 25.13 | .1360 | 120.8 | 2.234 | 36.06 |
| Ethylbenzene | 25.13 | .1345 | 129.7 | 2.236 | 38.26 |
| Apparatus No. 4 | $r_1 = 0.1927 - 0.1932$ $r = 0.5033 - 0.5072$ | | | | |
| Nitrobenzene | 25.13 | 0.2011 | 82.90 | 3.205 | 25.51 |
| Carbon bisulfide | 25.23 | .2584 | 121.00 | 3.197 | 47.95 |
| Carbon tetrachloride | 25.07 | .5872 | 48.37 | 3.206 | 43.44 |

[7] Von Lerch, *Ann. Physik*, **9**, 434 (1902).

[8] Clark, *Proc. Am. Acad.*, **41**, 361 (1906).

[9] Harkins and Humphrey, THIS JOURNAL, **38**, 236 (1916).

[10] Reynolds, *J. Chem. Soc.*, **119**, 460 (1921).

TABLE III

INTERFACIAL TENSIONS AGAINST MERCURY

| Organic liquid | Temp., °C. | Dens. diff. | $H_2$, mm. | $\frac{1}{r_1} - \frac{1}{r_2}$ | $S_{23}$, dynes/cm. |
|---|---|---|---|---|---|
| | Apparatus No. 4 | $r_1 = 0.1927 - 0.1932$ | | | |
| | | $r_2 = 0.5033 - 0.5072$ | | | |
| Water | 25.08 | 12.537 | 19.47 | 3.199 | 374.2 |
| Benzene | 25.13 | 12.660 | 18.34 | 3.199 | 355.5 |
| Nitrobenzene | 25.09 | 12.336 | 18.20 | 3.199 | 344.1 |

ful work of Harkins can be made quickly and easily with this double capillary apparatus. The use of the double capillary apparatus presents no special difficulties. It does, in fact, possess some advantages over the single capillary. The position of no flat meniscus need be determined. This allows a greater degree of accuracy in measuring the height of the mercury column, which is a very outstanding source of error with a liquid so dense.

Interfacial tension data obtained with the double capillary method are given in Tables I, II and III.

## Summary

Two new types of apparatus have been described for making interfacial tension measurements by the capillary rise method. These are the only methods so far devised for securing accurate values of the interfacial tensions where only small amounts of the liquid are available. The first type of apparatus gives good results without the need of determining carefully the density of the organic liquid. The second type gives very accurate results provided the density is known or is determined with precision. The interfacial tension values of a number of standard reference liquids have been determined with these apparatus and the results show good agreement with the most generally accepted of those reported in the literature.

ANN ARBOR, MICHIGAN

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND THE CHEMICAL INSTITUTE OF THE FORSTLICHE HOCHSCHULE, HANN-MÜNDEN, GERMANY]

# GAMMA-FERRIC OXIDE HYDRATE

BY OSKAR BAUDISCH AND WERNER H. ALBRECHT

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In an earlier communication one of the authors[1] has published results concerning the magnetic and crystallographic investigations of the products formed by the oxidation of ferrous bicarbonate solutions, and has shown further that γ-ferric oxide hydrate is formed on oxidizing ferrous ammonium sulfate solutions with iodates in the presence of thiosulfates.[2] Since this γ-hydrate is free from impurities and forms on dehydration ferromagnetic γ-ferric oxide, a new proof of the existence of a ferromagnetic cubic ferric oxide was established, which was still doubted by some authors despite the work of Sosman, Baudisch and Welo, Böhm, and others.

The x-ray photographs of the compounds which were obtained by the oxidation of ferrous bicarbonate solutions gave the diagram of the α-hydrate only. The compounds were also, in general, magnetically identical with one another. But some of the preparations, which were obtained by *slow oxidation* in air (weeks and months), not only showed differences among themselves, but also as compared with the compounds which were obtained by rapid oxidation (passing air through, or adding hydrogen peroxide). It was at that time suggested that a "ferrit" formation[3,4] and also that the presence of a small amount of divalent iron, were responsible for these properties.

We therefore repeated this slow oxidation and found that the precipitate obtained was not homogeneous, but contained a mixture of α- and γ-hydrates. They can be separated from each other since the γ-hydrate is formed as a dark brown crust on the surface of the solution, while the α-hydrate is formed in the solution itself as a finely-divided yellow precipitate on the bottom of the vessel. On drying the preparations, however, a part of the γ-hydrate is changed into γ-oxide, which is in accordance with the increase of the magnetic susceptibility.

Schickor[5] has recently described similar experiments, so that we can content ourselves with confirming his results, without bringing in further experimental material. He also makes the suggestion that an intermediate green labile ferrous-ferric complex is necessary for the formation of γ-ferric oxide hydrate.

Our further experiments, which were completed in the main by the

[1] Albrecht, *Ber.*, **62,** 1475 (1929).

[2] Hahn and Hertrich, *ibid.*, **56,** 1729 (1923).

[3] Hilpert, *Z. anorg. Chem.*, **169,** 273 (1928).

[4] Krause, *Ber.*, **42,** 2248 (1909); *Z. anorg. allgem. Chem.*, **197,** 301 (1931).

[5] Schickor, *Z. anorg. allgem. Chem.*, **191,** 322 (1930).

end of 1929, but which have not yet been published for various reasons, were based on the following considerations.

One of us has shown in earlier work[6] that in catalytic oxidations with the aid of iron salts, the oxygen used for the oxidation becomes temporarily activated, becoming coördinatively linked in an intermediate iron complex. Such "active" iron complexes could be identified.[7] This supposition contradicts two other theories. Manchot, as the leading representative of one, stipulates the formation of an intermediate iron peroxide, while Wieland, as the supporter of the other, supposes the formation of intermediary hydrogen peroxide. An exact proof for the existence of either the one or the other is lacking at the present time,[8] while the facts can be just as well explained by the aid of Baudisch's oxygen-complex theory, with the further advantage that complexes of which oxygen is a member are known with iron as well as with cobalt. If such a complex decomposes on further oxidation, one should expect that ferric oxide hydrate of another structure would be formed in this decomposition, as when, in the direct oxidation of a ferrous salt, the ferric salt formed decomposes by hydrolysis into ferric oxide hydrate and acid.

This theory explains the following experiment very well. If ferrous chloride solution is oxidized at ordinary temperatures (about 18°), whether quickly or slowly, only $\alpha$-hydrate is formed. If, however, the oxidation is carried out *slowly* at a somewhat higher temperature (40–50°) while the solution is being stirred slowly (a saturated solution diluted to one-half), a considerable percentage of $\gamma$-hydrate is formed. At temperatures from 90–100° $\alpha$-hydrate is obtained with slow as well as with rapid oxidation. The self-complex formation of ferrous chloride solution at higher temperatures has been shown as probable by other investigators,[9] and Chandra[10] has succeeded in isolating polynuclear ferrous–ferric complexes as their alkali salts by the partial oxidation of ferrous salt solutions.

An attempt was then made to obtain pure $\gamma$-oxide hydrate by oxidation following the addition of suitable complex-forming compounds to ferrous salt solutions. It has been shown that nitrogen-containing compounds are especially suitable, above all pyridine. As can be seen from the experimental part, it was possible to obtain pure $\gamma$-oxide hydrate by the addition of pyridine to ferrous chloride solutions. It has been shown, moreover, that not only the addition of a suitable complex-forming compound, but also the nature of the anions in the salt solution, is of impor-

[6] Baudisch, *Naturwissenschaften*, **16**, 542 (1928); see also Baudisch and Welo, *J. Biol. Chem.*, **61**, 261 (1924).

[7] *Biochem. Z.*, **232**, 35 (1931).

[8] *Cf.* Abegg's "Handbuch der anorganischen Chemie," Vol. IV, 3d. ed., II, Teil B, pp. 8 *et seq.*

[9] Abegg, *Z. Elektrochem.*, **10**, 77 (1904).

[10] Chandra, Inaugural dissertation, Friedrich Wilhelm University, Berlin, 1913.

tance for the formation of γ-oxide hydrate; *i. e.*, it was impossible to obtain γ-oxide hydrate from ferrous sulfate or ferrous fluoride solutions. A γ-oxide formation from ferric nitrate solutions was not expected and not found, as the oxidizing power of nitric acid is too great for the formation of any kind of intermediate products with the desired properties.

In further preparations of γ-oxide hydrate, the addition of sodium azide to the ferrous chloride solutions was found to be of great advantage. The question as to whether this addition of sodium azide to the ferrous salt solutions forms a complex cannot be definitely answered from our experimental material. The red color of the solution points to the formation of an iron azide.[11] In oxidations at a higher temperature hydrazoic acid, which can be recognized by its odor, is given off abundantly. It is interesting to note that the formation of γ-hydrate does not commence until the solution is already partly oxidized, and the originally alkaline solution ($P_H$ 8 to 10) has become weakly acid. The formation of γ-hydrate first starts from a $P_H$ of 6.5 to *ca.* 2.0. It seems then that the formation of γ-hydrate is dependent also on the hydrogen-ion concentration, for it is always found that γ-hydrate is formed only in weakly acidic solutions ($P_H$ 2–6.5). This observation is in agreement with that of Krause,[4] who is of the opinion that his "metaferric hydroxide" ("eisenige Säure") with the isoelectric point $P_H$ 5.2 is identical with the γ-hydrate.

## Experimental Part

The purest iron powder, prepared by I. G. Farbenindustrie A.-G.[12] from iron-pentacarbonyl, was used in excess, being dissolved in the corresponding acid until the solutions reacted neutral to Congo paper. The oxidations were then made with these solutions.

**Hydrochloric Acid Solutions.**—The solutions were still more weakly acid ($P_H$ 4 to 5). On oxidation by means of air, oxygen, or hydrogen peroxide, a yellow precipitate of α-hydrate separated out. On slower oxidation at a somewhat higher temperature with stirring, a mixture of α- and γ-hydrates was formed.

One hundred cc. of the concentrated ferrous chloride solution was diluted with 100 cc. of water and 20 cc. of the purest Merck pyridine added. A green precipitate came out which, however, dissolved upon shaking. On passing air or oxygen through the mixture an orange-red precipitate of γ-hydrate was formed. On the addition of pyridine the $P_H$ of the solution rose to about 6–6.4 and then remained practically constant after the oxidation. The formation of γ-hydrate was proved by the fact that the precipitate was then free from divalent iron and gave a ferromagnetic ferric oxide on dehydration at 280–290°. If the solution to which pyridine had been added was then heated on the water-bath and air passed through, α-hydrate was formed. α-Hydrate was also formed on oxidizing the pyridine-containing solution with hydrogen peroxide. Changing the concentration of the solutions of ferrous chloride or of pyridine did not change the oxidation product. If an excess of pyridine was added to the solution, *i. e.*, 50 cc. of concentrated ferrous chloride solution and 50 cc. of pyridine, the

[11] Salomea Lorie, Inaugural dissertation, "Stickstoffwasserstoffsäure und ihre anorganischen Verbindungen," Zürich, 1912.

[12] At this point we should like to thank the I. G. Farbenindustrie A.-G. for their kind supply of the preparations used in this research.

solution solidified to a gray-green mass. An attempt to oxidize this gray-green mass with air or oxygen yielded no satisfactory results. Dark brown products are formed which are very difficult to wash free of chlorides and pyridine. If, however, the gray-green precipitate is shaken with much water before oxidizing, most of it goes into solution, forming a green color, and is oxidized to $\gamma$-hydrate by passing through air or oxygen.

If piperidine or ammonia was added to the ferrous chloride solution instead of pyridine, $\gamma$-hydrate was never formed, even under the same conditions as when pyridine was used.

When the ferrous chloride solution was added to a 10% sodium azide solution, the green solution became red and alkaline ($P_H$ 10). Upon passing through air or oxygen a yellowish-red precipitate of $\alpha$-hydrate was formed, the $P_H$ changing meanwhile to neutral or weakly acidic. The filtrate from this precipitate was warmed on the steam-bath and more oxygen passed through. A yellowish-red precipitate of $\gamma$-hydrate was formed, the solution becoming colorless and strongly acid. The reaction was quantitative. If a large amount of sodium azide was added to the solution, the precipitate obtained on oxidation always contained chlorides and nitrogen. The following method of precipitation proved to be very satisfactory; 50 cc. of ferrous chloride solution ($P_H$ 5) was added to 50 cc. of water and 20 cc. of 10% sodium azide solution poured in. The resulting red solution had a $P_H$ of 8.9. After oxidation by passing oxygen through at water-bath temperature, the now colorless solution had a $P_H$ of 2.4. The reddish-yellow precipitate was easily filtered and washed, then identified as $\gamma$-hydrate.

Analogous experiments on solutions containing excess of iron were carried out with hydrobromic, hydriodic, hydrofluoric, sulfuric and nitric acids.

Upon dissolving iron in nitric acid, an oxidation set in immediately, and upon precipitation with organic or inorganic bases red oxide hydrates were formed.

Moreover, no $\gamma$-hydrate was formed on oxidizing ferrous fluoride and ferrous sulfate under the same conditions as with the ferrous chloride, while in the cases of the bromide and iodide positive results were obtained. No doubt the ferrous bromide solution behaved in a manner exactly analogous to the ferrous chloride solution. On oxidation of the iodide solutions, the precipitates which formed always contained iodides.

## Magnetic Measurements

The mass susceptibilities of a series of preparations made from iron chloride by oxidation in the presence of pyridine were determined.[1]

| No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $\chi \times 10^6$ | 100 | 215 | 115 | 308 | 46 |
| Moles of $H_2O$ | 1.22 | .... | 2.50 | 1.52 | 1.73 |

All the preparations with the exception of preparation 5 contained divalent iron. This latter was dehydrated slowly at different temperatures and from time to time its water content and magnetic susceptibility were measured:

| Time of heating, hrs. | $T$, °C. | $\chi \times 10^6$ | Amp. | Moles of $H_2O$ |
|---|---|---|---|---|
| 20 | 110 | 30 | 1, 2, 3 | 1.76 |
| 6 | 140–185 | 33 | 1, 2 | 1.64 |
| 2 | 240–280 | 538 | 0.50 | 0.21 |
| | | 335 | 1.00 | |
| | | 218 | 2.0 | |

| Time of heating, hours | $T$, °C. | $\chi \times 10^6$ | Amp. | Moles of $H_2O$ |
|---|---|---|---|---|
| 2 | 205 | 121 | 1.00 | 1.41 |
| | | 96 | 2.00 | |
| | | 84 | 3.00 | |
| 2 | 195 | 209 | 0.50 | 1.37 |
| | | 186 | 1.00 | |
| | | 140 | 2.00 | |
| 2 | 200 | 506 | 0.50 | 1.40 |
| | | 332 | 1.00 | |
| | | 284 | 1.50 | |
| 24 | 200 | 1870 | 0.50 | 1.03 |

A sample of the original material was sealed off in a hard glass tube and heated under water for two hundred hours. The resulting product was bright red, still contained, after drying with acetone and ether, 1.1 mole of water and its magnetic susceptibility was $\chi = 40 \times 10^{-6}$.

Further, two compounds which had been prepared by oxidation at water-bath temperature in the presence of sodium azide were magnetically measured. Both were free from divalent iron, contained 2.4 and 2.1 moles of water, respectively, and their magnetic susceptibilities were 56 and 55 $\times 10^{-6}$. Upon heating to 280–290° they became strongly ferromagnetic.

## Summary

1. Under certain conditions ferrous bicarbonate solution is autoxidized to γ as well as α-ferric oxide hydrate.

2. The oxygen-complex theory of Baudisch was supported by the following new preparations of γ-$Fe_2O_3 \cdot H_2O$ and γ-$Fe_2O_3$. (*a*) γ-$Fe_2O_3 \cdot H_2O$ is formed by air-oxidation of ferrous chloride solutions under conditions where auto-complex-formation is favored. (*b*) In presence of certain organic nitrogen-containing compounds, the oxidation of ferrous chloride solution with air forms quantitatively γ-$Fe_2O_3 \cdot H_2O$. (*c*) γ-$Fe_2O_3 \cdot H_2O$ is formed by air-oxidation of ferrous chloride solutions in presence of sodium azide and under a certain $P_H$.

3. The newly synthesized $Fe_2O_3 \cdot H_2O$ preparations were magnetically measured.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

# GERMANIUM. XXXVIII. THE PARACHORS OF CERTAIN COMPOUNDS OF GERMANIUM AND THE ATOMIC CONSTANT FOR GERMANIUM

N. V. SIDGWICK AND A. W. LAUBENGAYER

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## Introduction

From a consideration of the regularities in the differences between the parachors of neighboring elements in the periodic system, Sugden[1] predicted that the atomic parachor for germanium should be 36, but no experimental data have been available to verify the prediction. Metallic germanium melts at 958.5° and is easily oxidized, so that direct determination of its parachor is not readily accomplished. However, the element does form several compounds which are liquid under ordinary conditions and which lend themselves to such measurements.

In the present investigation carefully purified quantities of germanium tetrachloride, germanium tetrabromide, germanium tetraethyl and germanium tetraethoxyl were prepared, their densities and surface tensions were determined, and their parachors were calculated. By use of the accepted constants given by Sugden[2] for the other elements present in each compound the atomic parachor for germanium was calculated.

## Experimental

### A. Preparation and Purification of Materials

**Benzene.**—Thiophene-free benzene was purified by repeated freezing and by distillation over sodium. It melted at 5.4°. (All temperatures given are corrected.)

***m*-Xylene.**—Kahlbaum's "purest" *m*-xylene was distilled over sodium. The middle fraction selected distilled at 136–139°.

**Germanium Tetrachloride,** $GeCl_4$.—This was prepared from pure germanium dioxide and hydrochloric acid.[3] The tetrachloride was allowed to stand over solid anhydrous sodium carbonate to remove traces of hydrogen chloride and was further purified by fractional distillation in a vacuum fractionation apparatus.[4] The purified sample had a vapor tension at 0° of 25 mm. (24.3 mm. reported by Laubengayer and Tabern).[5]

**Germanium Tetrabromide,** $GeBr_4$.—The tetrabromide was prepared by the action of hydrobromic acid on pure germanium dioxide[6] and was purified by fractional distillation. The middle fraction boiled at 186° (186.5° reported by Brewer and Dennis).[7]

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[1] Sugden, "The Parachor and Valency," George Rutledge and Sons, Ltd., London, 1930, p. 184.

[2] Sugden, *ibid.*, p. 38.

[3] Tabern, Orndorff and Dennis, THIS JOURNAL, **47,** 2039 (1925).

[4] Laubengayer and Corey, *J. Phys. Chem.*, **30,** 1043 (1926).

[5] Laubengayer and Tabern, *ibid.*, **30,** 1047 (1926).

[6] Laubengayer and Brandt, THIS JOURNAL, **54,** 549 (1932).

[7] Brewer and Dennis, *J. Phys. Chem.*, **31,** 1105 (1931).

**Germanium Tetraethyl, $Ge(C_2H_5)_4$.**—Germanium tetraethyl was prepared by the action of magnesium ethyl bromide on germanium tetrachloride[8] and was purified by fractional distillation. The preparation that was used boiled at 162–163° (162.5–163° reported by Tabern, Orndorff and Dennis).[8]

**Germanium Tetraethoxyl, $Ge(OC_2H_5)_4$.**—This substance was obtained by the action of sodium ethylate on germanium tetrachloride.[8] The sample boiled at 187° (185–187° reported by Tabern, Orndorff and Dennis).[8]

**B. Measurement of Density.**—The density determinations were made by a pycnometric method. Germanium tetrachloride, tetrabromide and tetraethoxyl are readily hydrolyzed by the moisture of the air and hence the ordinary type of pycnometer could not be used. One of special design was made by sealing a glass bulb of about 10-cc. capacity to a graduated capillary tube 5-cm. long which was connected through a stopcock to an interchangeable ground-glass slip joint so that the bulb could be fitted to the vacuum fractionation chain[4] when the sample was to be transferred. This density bulb was calibrated with mercury at the temperature of the density determinations. The tared calibrated bulb was filled with the sample by distillation in dry air or *in vacuo*, eliminating all chance for hydrolysis and insuring high accuracy. A thermostat held constant within 0.1° provided proper temperature control. All weighings were corrected to vacuum.

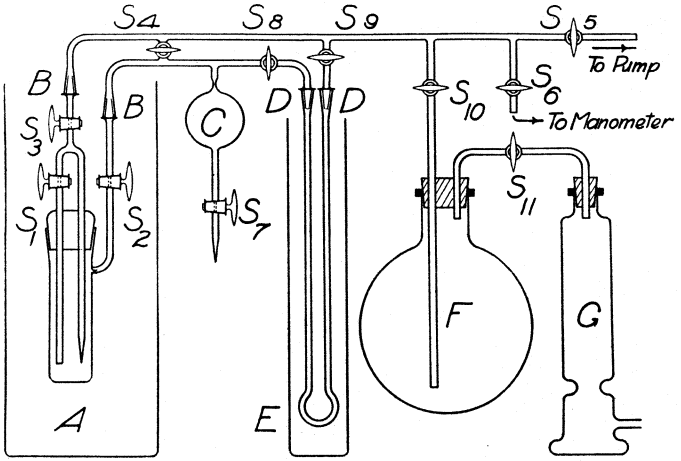


Fig. 1.

**C. Measurement of Surface Tension.**—The surface tension measurements were made by the maximum bubble pressure method described by Sugden.[9] Since some of the substances investigated were very sensitive to moisture it was found necessary to modify the apparatus in order to prevent breakdown of the compound during transfer or while the measurements were in progress. Figure 1 shows the essential details. A is the bubbler tube constructed according to Sugden's directions. It is provided with stopcocks $S_1$, $S_2$ and $S_3$ and the interchangeable ground glass slip joints B, B, and is immersed in the same thermostat that is used for the density determinations. C is a mercury aspirator bulb of about 150-cc. capacity. The manometer E is filled half full of purified xylene of known density and is immersed in a thermostatic ba[th]

[8] Ref. 3, p. 2043.

[9] Ref. 1, p. 208.

held at 25 ± 0.1°. Pressure differences are measured by means of a cathetometer reading to 0.01 mm. E is connected to the apparatus by the interchangeable slip joints D, D, through the stopcocks $S_8$ and $S_9$. This construction makes it possible to remove the manometer, clean it, and refill it before each experiment, and if $S_8$ and $S_9$ are kept closed except when actual measurements are being made the chances for contamination of the manometric liquid are reduced to a minimum. F is a five-liter balloon flask containing phosphorus pentoxide and is used as a drying chamber and storage reservoir for the gas that is to be drawn through the bubbler. G is a calcium chloride tower for the preliminary drying of the gas. $S_5$ leads to an efficient vacuum pump and the system can be connected to a mercury manometer through $S_6$.

When the surface tension of a sensitive liquid that has an appreciable vapor tension at room temperature is to be measured, the bubbler tube A is detached and connected to the vacuum fractionation chain[4] containing the purified sample. A is then evacuated, dried and filled with the sample by low temperature vacuum distillation. If the liquid is not volatile at room temperature it may be purified and distilled into A in a current of dry inert gas. This procedure eliminates the possibility of breakdown of the sample during transfer. A is reattached to the surface tension apparatus and the entire system between $S_2$, $S_3$, $S_7$ and $S_{10}$ is evacuated, $S_4$, $S_8$ and $S_9$ being open. F is filled with a gas which does not react with the particular sample being investigated. $S_{10}$ is opened slowly and the dry gas is admitted. $S_8$, $S_9$ and $S_{10}$ are closed and the apparatus is again evacuated to remove any traces of xylene vapor. Then $S_2$ and $S_3$ are opened, and dry gas from F is allowed to enter by opening $S_{10}$ slowly. $S_4$ is closed and $S_8$ and $S_9$ are opened. The mercury aspirator is started and the procedure from this point on is that described by Sugden.

In order to allow evacuation of the apparatus it is necessary to use a lubricating grease on the stopcocks and slip joints, and some concern was felt about possible contamination of the sample. It was found, however, that if a good high-vacuum lubricant was applied sparingly, no contamination occurred, as was shown by the consistent results secured when benzene was used to calibrate the apparatus and by the fact that determinations of the surface tension of successive samples of the same substance always agreed well.

As a final test of the apparatus the parachor for pure benzene was determined at 30 and 50°. At 30° the value secured was 206.03 while at 50° it was 206.5. This showed that the apparatus described was satisfactory for the measurement of surface tension.

The apparatus was checked frequently during the course of the investigation by determining the surface tension of pure benzene.

**D. Experimental Results.**—The results found are given in Table I together with the molecular parachors [P], calculated according to the method of Sugden.[10] The atomic parachor for germanium was obtained

TABLE I

EXPERIMENTAL RESULTS

| Substance, germanium | Temp., °C. | Density | Surface tension | [P] observed | Σ[P] | Atomic parachor of germanium |
|---|---|---|---|---|---|---|
| Tetrachloride | 30 | 1.8443 | 22.44 | 253.2 | 217.2 | 36.0 |
| Tetrabromide | 30 | 3.1002 | 35.51 | 308.9 | 272.0 | 36.9 |
| Tetrabromide | 50 | 3.0516 | 33.70 | 309.7 | 272.0 | 37.7 |
| Tetraethyl | 30 | 0.9850 | 22.96 | 419.5 | 380.4 | 39.1 |
| Tetraethoxyl | 30 | 1.1278 | 23.00 | 490.8 | 460.4 | 30.38 |

[10] Ref. 1, p. 30.

in each case by subtracting the parachor increment, $\Sigma[P]$, due to all other atoms present in the molecule, from the molecular parachor.

## Discussion of Results

The values obtained for the atomic parachor of germanium in the case of the tetrachloride, tetrabromide and tetraethyl are fairly consistent, and the average of these values, 37.4, is close to the 36 predicted by Sugden. Germanium tetraethoxyl gives a low value which probably may be accounted for by the difference in the type of compound. Simple alcohols give negative anomalies due to association, and the similarity in structure might lead one to expect that germanium tetraethoxyl should also show a negative anomaly.

The values for the germanium compounds are paralleled to some extent by the data reported for corresponding silicon compounds by Sugden and Williams.[11] The values for the methoxy and ethoxy compounds are lower than those reported for the tetraalkyls. Sugden and Williams also found that the parachors of silicon tetramethoxyl and silicon tetraethoxyl increase with the temperature while the tetraalkyls give a constant for silicon independent of temperature.

TABLE II

VALUES FOR SILICON COMPOUNDS

| Substance, silicon | [P] obs. | $\Sigma[P]$ | Atomic parachor of silicon |
|---|---|---|---|
| Tetraethoxyl | 487.6 | 460.4 | 27.2 |
| Tetramethoxyl | 330.9 | 304.4 | 26.5 |
| Tetraethyl | 412.1 | 380.4 | 31.7 |
| Tetrapropyl | 565.3 | 536.4 | 28.9 |
| Tetraphenyl | 787.5 | 760.0 | 27.5 |

On the other hand it is remarkable that the borates show no corresponding anomaly, but give values[12] of the parachor of boron agreeing with that obtained from the trichloride.[13]

TABLE III

VALUES FOR BORON COMPOUNDS

| Substance | [P] obs. | [P] | Atomic parachor of boron |
|---|---|---|---|
| Boron trichloride | 178.8 | 162.9 | 15.9 |
| Methyl borate | 243.7 | 228.3 | 15.4 |
| Ethyl borate | 363.1 | 345.3 | 17.8 |

## Summary

The molecular parachors of germanium tetrachloride, germanium tetrabromide, germanium tetraethyl and germanium tetraethoxyl have been

[11] Sugden and Williams, *J. Chem. Soc.*, 126 (1931).

[12] Etridge and Sugden, *ibid.*, 989 (1928).

[13] Mills and Robinson, *ibid.*, 1823 (1927).

determined and the atomic parachor for germanium calculated. Good agreement with the value predicted by Sugden was observed. The anomaly obtained in the case of germanium tetraethoxyl is explained by the difference in structure.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 299, AND FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

# THE REACTION RATE OF POTASSIUM IODIDE WITH DIBROMIDES OF THE ETHYLENE BROMIDE TYPE

BY ROBERT T. DILLON

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## Introduction

In a method for analyzing mixtures of the three normal butenes it was necessary[1] to utilize the specific reaction rate constants of the corresponding dibromobutanes with potassium iodide in methanol at 75°. The stoichiometric equation involved was expressed by equation (1)

$$C_4H_8Br_2 + 2KI = C_4H_8 + 2KBr + I_2 \quad (1)$$

Kinetically the reaction was readily followed by the titration of the iodine. It was pointed out in this article that the equation could equally well, and more probably should, have been expressed as follows

$$C_4H_8Br_2 + 3KI = C_4H_8 + 2KBr + KI_3 \quad (2)$$

which differs from the first form only by equation (3)

$$I_2 + KI = KI_3 \quad (3)$$

In an aqueous solution this reaction of iodine with potassium iodide takes place completely; but in an alcoholic solution this is perhaps questionable and for this reason the first form of the dibromide reaction was used in the previous paper. In this article, however, are given calculations made from the experimental data of van Duin[2] which show that equation (3) is evidently complete even in alcoholic solutions and, therefore, that one mole of dibromide[3] reacts with three moles of potassium iodide according to equation (2). Hence this stoichiometric equation should be the basis for the differential equations expressing the velocity of the reaction.

However, the use of either equation would not alter the result previously found, namely, that kinetically the reaction is one of the second order, the rate being proportional to the first power of the concentrations of both

[1] Dillon, Young and Lucas, THIS JOURNAL, **52**, 1953 (1930).

[2] Van Duin, *Rec. trav. chim.*, **43**, 341 (1924).

[3] The term "dibromide" as used herein is understood to mean only ethylene bromide and its homologs, or their substituted derivatives.

the dibromobutane and the potassium iodide.[4] This is in accord with the results of Biilmann,[5] who found that the reaction of 2,3-dibromopropanoic acid with potassium iodide in dilute sulfuric acid at 25° was also of the second order. In addition it may be mentioned that Slator[6] has found that the reactions of ethylene bromoiodide and ethylene iodide with potassium iodide are very rapid. From this it follows that the comparatively slow reaction of ethylene bromide, presumably involving either one or both of the preceding compounds as an intermediate product, would not be of the third order, but of the first or second. On the other hand, van Duin[2,7] discusses the work of Biilmann and Slator, rejects their conclusions and reports that the reaction of dibromides[8] with potassium or sodium iodide is of the third order.

For this reason, it was deemed desirable to extend somewhat the investigations previously described. The work was aided financially by a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington. The author is indebted to Professor Howard J. Lucas for his valuable criticisms and suggestions.

## Experimental

The procedure and technique used in the rate measurements are as described in the previous work.[1] To this description the following further details should be added. The purified ethylene and propylene bromide boiled, respectively, at 130.3–130.5° and 140.0° at 743–744 mm. The small corrections for the disappearance of iodine due to its reaction with impurities remaining in the purified alcohol solvents were made with greater accuracy for the experiments involving short intervals of time. For the preparation of the reaction mixtures the dried potassium iodide was weighed into the volumetric flask and the salt completely dissolved by shaking with almost the required volume of solvent. The solution was brought to a temperature of 20° in a thermostat, the required amount of dibromide was added from a weighing pipet and the solution quickly made up to the exact volume. The solution was next pipetted into the reaction tubes. They were then sealed, placed in a light-tight thermostat which was regulated to within ±0.03° of the desired temperature, removed at appropriate intervals and analyzed by titration with 0.02

[4] Since the potassium iodide concentration is seven to twelve times that of the dibromide, calculation of the second order constant according to either stoichiometric equation leads to substantially the same numerical value of the constant. (See Table IV.)

[5] Biilmann, *Rec. trav. chim.*, **36**, 319 (1917).

[6] Slator, *J. Chem. Soc.*, **85**, 1697 (1904).

[7] Van Duin, *Rec. trav. chim.*, **45**, 345 (1926).

[8] Van Duin tested the order only with ethylene bromide but his conclusions were generalized for all dibromides.

$N$ thiosulfate. The second and third order specific reaction rate constants were calculated from the analytical data by means of the usual integrated expressions for $k_2$ and $k_3$.[9] They are, on the basis of equation (2)

$$k_2 = \frac{2.303}{t(a - 3b)} \log_{10} \frac{b(a/b - 3\varphi)}{a(1 - \varphi)} \quad (4)$$

$$k_3 = \frac{1}{t(a - 3b)^2} \left[ - \frac{3\varphi(a - 3b)}{a(a/b - 3\varphi)} + 2.303 \log_{10} \frac{b(a/b - 3\varphi)}{a(1 - \varphi)} \right] \quad (5)$$

where $t$ is the time in hours, $a$ and $b$ are the initial concentrations of potassium iodide and dibromide, respectively, in moles per liter at 20° and $\varphi$ is the fraction of the dibromide which had reacted at the time $t$. The values of $k_2$ and $k_3$ are thus expressed in (hours)$^{-1}$ (moles/liter)$^{-1}$ and (hours)$^{-1}$ (moles/liter)$^{-2}$, respectively.

The times involved in the rate measurements were always taken from the time of immersion of the tubes in the thermostat. The reactions were in all cases so slow at 20° that the interval between the addition of the dibromide and the insertion of the tubes into the thermostat, namely, twenty to thirty minutes, was entirely negligible. The concentration of the dibromides was kept essentially constant throughout the work since the rate is undoubtedly proportional to the first power of this value.[1,2,5] Measurements were made with at least two different initial concentrations of the potassium iodide in order to determine the dependence of the reaction rate upon the concentration of this reactant.

## Results and Discussion

**Influence of Iodine upon the Rate of Reaction.**—This influence is shown in Table I. Thus, when either second or third order constants are calculated on the basis of the stoichiometric equation (1) the presence of some initial iodine in the reaction mixture leads to lower values of the constants than in the absence of this initial iodine (*e. g.*, 2.68 and 0.648 as against 3.04 and 0.727 without the iodine). As may be seen, these values differ by approximately 10% which corresponds with the decrease in iodide ion concentration brought about by the introduction of iodine into the reaction mixture in experiment B. However, when second order constants are calculated on the basis of equation (2) in which the formation of triiodide ion is taken into account, the values are practically identical (*e. g.*, 0.742 and 0.734). It is perhaps needless to say that in these last calculations a correction is necessary for the effect of this initial iodine upon the concentration of the iodide ion. The results indicate that equation (2) is the correct stoichiometric form to use in the calculation of the specific rate constants for this reaction.

[9] The expression for $k_3$ in the preceding article[1] (equation 17) is incorrectly printed, the logarithm applying only to the first term within the brackets.

TABLE I

INFLUENCE OF TRIIODIDE FORMATION ON THE REACTION RATE OF *p*-$NaSO_3C_6H_4CHBr$-$CHBrCOONa$ WITH POTASSIUM IODIDE[a]

| KI, 0.25 *M* Dibromide, 0.025 *M* | Time, min. | Constants × $10^3$ $k_3$[b] | $k_2$[c] | $k_2$[d] |
|---|---|---|---|---|
| A. Without initial iodine | 931 | 3.03 | 0.742 | 0.749 |
| | 1721 | 3.06 | .741 | .752 |
| | 2586 | 3.08 | .718 | .739 |
| | 3856 | 2.99 | .705 | .727 |
| | Average | 3.04 | .727 | .742 |
| B. With initial iodine (≦0.1 initial KI) | 932 | 2.75 | 0.675 | 0.757 |
| | 1724 | 2.71 | .659 | .745 |
| | 2587 | 2.68 | .644 | .735 |
| | 3858 | 2.58 | .613 | .705 |
| | Average | 2.68 | 0.648 | 0.734 |
| Difference between A and B, % | | 12.6 | 11.5 | 1.1 |

[a] These experimental data were taken from the work of van Duin (Ref. 2).

[b] On the basis of equation (1):

$$k_3 = \frac{1}{t(a-2b)^2}\left[-\frac{2\varphi(a-2b)}{a(a/b-2\varphi)} + 2.303\log_{10}\frac{b(a/b-2\varphi)}{a(1-\varphi)}\right]$$

The values were calculated and reported by van Duin.

[c] On the basis of equation (1)

$$k_2 = \frac{1}{t(a-2b)}\log_{10}\frac{b(a/b-2\varphi)}{a(1-\varphi)}$$

[d] On the basis of equation (2): $k_2$ from equation (4).

**Order and Temperature Coefficients of the Reaction Rates.**—The detailed data relating to the reaction rate measurements of ethylene bromide with potassium iodide in methanol at 30.00, 59.72 and 74.93° are given in Table II. Table III gives the data for propylene bromide at 59.72 and 74.93°. The values of $k_2$ and $k_3$ were calculated from equations (4) and (5), respectively. The same terms and units are used in these tables

TABLE II

REACTION RATE CONSTANTS OF ETHYLENE BROMIDE WITH POTASSIUM IODIDE IN 99% METHANOL

Temp. 30.00°

| KI, 0.2152 *M* $C_2H_4Br_2$, 0.02450 *M* Time | $\varphi$ | $k_2$ | $k_3$ | KI, 0.1469 *M* $C_2H_4Br_2$, 0.02529 *M* Time | $\varphi$ | $k_2$ | $k_3$ |
|---|---|---|---|---|---|---|---|
| 91.4 | 0.1757 | 0.0101 | 0.0484 | 90.7 | 0.1191 | 0.0099 | 0.0702 |
| 100.8 | .1925 | .0102 | .0490 | 100.0 | .1318 | .0103 | .0711 |
| 115.3 | .2154 | .0101 | .0490 | 114.5 | .1485 | .0100 | .0712 |
| 126.2 | .2340 | .0102 | .0496 | 125.4 | .1610 | .0100 | .0715 |
| 136.9 | .2498 | .0102 | .0497 | 136.2 | .1750 | .0101 | .0728 |
| 151.5 | .2719 | .0102 | .0500 | 150.8 | .1911 | .0101 | .0731 |
| 174.4 | .3061 | .0103 | .0508 | 173.7 | .2163 | .0102 | .0740 |
| | Average | 0.0102 | 0.0495 | | Average | 0.0101 | 0.0720 |

TABLE II (*Concluded*)

Temp. 59.72°

KI, 0.2237 *M*; $C_2H_4Br_2$, 0.02655 *M*

| Time | $\varphi$ | $k_2$ | $k_3$ |
|---|---|---|---|
| 8.25 | 0.3985 | 0.299 | 1.46 |
| 11.25 | .4914 | .299 | 1.49 |
| 13.25 | .5420 | .297 | 1.50 |
| 15.25 | .5909 | .299 | 1.54 |
| 17.25 | .6332 | .301 | 1.57 |
| 20.25 | .6823 | .298 | 1.57 |
| 23.25 | .7268 | .298 | 1.61 |
| | Average | 0.299 | 1.53 |

KI, 0.1531 *M*; $C_2H_4Br_2$, 0.02864 *M*

| Time | $\varphi$ | $k_2$ | $k_3$ |
|---|---|---|---|
| 8.25 | 0.2863 | 0.292 | 2.10 |
| 11.25 | .3630 | .296 | 2.19 |
| 13.25 | .4099 | .299 | 2.26 |
| 15.50 | .4572 | .302 | 2.33 |
| 17.25 | .4890 | .303 | 2.37 |
| 20.25 | .5396 | .305 | 2.46 |
| 23.25 | .5795 | .302 | 2.49 |
| | Average | 0.300 | 2.32 |

Temp. 74.93°

KI, 0.2157 *M*; $C_2H_4Br_2$, 0.02200 *M*

| Time | $\varphi$ | $k_2$ | $k_3$ |
|---|---|---|---|
| 1.00 | 0.2347 | 1.29 | ... |
| 1.25 | .2884 | 1.32 | ... |
| 1.67 | .3661 | 1.35 | ... |
| 3.00 | .5564 | 1.39 | ... |
| | | 1.34 | |

TABLE III

REACTION RATE CONSTANTS OF PROPYLENE BROMIDE WITH POTASSIUM IODIDE IN 99% METHANOL

Temp. 59.72°

KI, 0.2208 *M*; $C_3H_6Br_2$, 0.02216 *M*

| Time | $\varphi$ | $k_2$ | $k_3$ |
|---|---|---|---|
| 17.50 | 0.04365 | 0.0118 | 0.0540 |
| 22.08 | .05381 | .0116 | .0531 |
| 25.50 | .06175 | .0116 | .0530 |
| 31.00 | .07306 | .0113 | .0520 |
| 41.75 | .09432 | .0110 | .0505 |
| 46.32 | .1031 | .0109 | .0502 |
| 51.58 | .1133 | .0108 | .0499 |
| 56.58 | .1228 | .0107 | .0497 |
| 66.00 | .1441 | .0110 | .0509 |
| | Average | 0.0113 | 0.0515 |

KI, 0.1827 *M*; $C_3H_6Br_2$, 0.02315 *M*

| Time | $\varphi$ | $k_2$ | $k_3$ |
|---|---|---|---|
| 21.00 | 0.04331 | 0.0116 | 0.0641 |
| 25.00 | .05110 | .0115 | .0640 |
| 30.83 | .06150 | .0114 | .0630 |
| 35.83 | .06648 | .0106 | .0590 |
| 45.25 | .08337 | .0107 | .0595 |
| 51.00 | .09117 | .0105 | .0582 |
| 57.00 | .1018 | .0104 | .0587 |
| 66.00 | .1286 | .0117 | .0658 |
| | Average | 0.0111 | 0.0615 |

Temp. 59.72°

KI, 0.1491 *M*; $C_3H_6Br_2$, 0.02444 *M*

| Time | $\varphi$ | $k_2$ | $k_3$ |
|---|---|---|---|
| 21.00 | 0.03651 | 0.0118 | 0.0788 |
| 25.00 | .04143 | .0114 | .0773 |
| 30.83 | .04861 | .0109 | .0742 |
| 35.83 | .05537 | .0108 | .0736 |
| 45.25 | .06911 | .0108 | .0736 |
| 51.00 | .07670 | .0107 | .0731 |
| 57.00 | .08511 | .0107 | .0734 |
| 66.00 | .1017 | .0111 | .0769 |
| | Average | 0.0110 | 0.0751 |

Temp. 74.93°

KI, 0.2170 *M*; $C_3H_6Br_2$, 0.02404 *M*

| Time | $\varphi$ | $k_2$ | $k_3$ |
|---|---|---|---|
| 17.87 | 0.1952 | 0.0580 | .. |
| 20.50 | .2179 | .0575 | .. |
| 26.08 | .2688 | .0581 | .. |
| 31.00 | .3105 | .0586 | .. |
| 42.05 | .3907 | .0585 | .. |
| 56.75 | 4.800 | .0584 | .. |
| | Average | 0.0582 | |

as indicated previously for these two equations except that the concentrations of potassium iodide and dibromide are indicated by KI and $C_2H_4Br_2$ (or $C_3H_6Br_2$) instead of by $a$ and $b$. As is evident, there is good agreement among the second order values both in individual experiments and in ones with different initial iodide concentrations, whereas the third order values show wide deviations.

Since the preceding section indicates that equation (2) is the correct one for these reactions in alcoholic solutions, this same method of calculation has been applied to the data previously published on the dibromobutanes.[1] The values of the reaction constants for all of the compounds investigated are summarized in Table IV. The table includes rate measurements of the reaction carried out in aqueous methanol and ethanol solutions in order to determine possible effects arising from the addition

TABLE IV

SUMMARY OF REACTION RATE CONSTANTS

| Temp., °C. | Dibromide (~0.022 $M$) | KI concn. ($M$) | Solvent wt. per cent. of methanol | Specific reaction rate constants $k_2$ | $k_3$ |
|---|---|---|---|---|---|
| 30.00 | $CH_2BrCH_2Br$ | 0.2152 | 99.2 | 0.0102 | 0.0495 |
| | | .1469 | 99.2 | .0101 | .0720 |
| | | .2207 | 63.0 | .0154 | |
| | | .1496 | 63.0 | .0157 | |
| 59.72 | $CH_2BrCH_2Br$ | .2237 | 99.0 | .299 | 1.53 |
| | | .1531 | 99.0 | .300 | 2.32 |
| | | .2240 | 72.0 | .402 | |
| | | .1516 | 72.0 | .411 | |
| | $CH_3CHBrCH_2Br$ | .2208 | 99.0 | .0113 | 0.0515 |
| | | .1827 | 99.0 | .0111 | .0615 |
| | | .1491 | 99.0 | .0110 | .0751 |
| | | .2194 | 72.0 | .0166 | |
| | | .1524 | 72.0 | .0169 | |
| | | .2225 | 68.3[a] | .0261 | |
| | | .1519 | 68.3[a] | .0260 | |
| | $CH_3CH_2CHBrCH_2Br$ | .2281 | 99.0 | .0148 (0.0147)[b] | |
| | $CH_3CHBrCHBrCH_3$ (meso) | .2287 | 99.0 | .00902 (.00896)[b] | |
| | (racemic) | .2281 | 99.0 | .00465 (.00462)[b] | |
| 74.93 | $CH_2BrCH_2Br$ | .2157 | 99.0 | 1.34 | |
| | $CH_3CHBrCH_2Br$ | .2170 | 99.0 | .0582 | |
| | $CH_3CH_2CHBrCH_2Br$ | .2298 | 99.0 | .0800 (.0773)[b] | 0.357[c] |
| | | .2296 | 99.0 | .0787 | |
| | | .1470 | 99.0 | .0811 (.0784)[b] | .567[c] |
| | $CH_3CHBrCHBrCH_3$ (meso) | .2217 | 99.0 | .0562 (.0544)[b] | .256[c] |
| | (meso) | .1461 | 99.0 | .0564 (.0545)[b] | .386[c] |
| | (racemic) | .2327 | 99.0 | .0301 (.0294)[b] | .130[c] |
| | (racemic) | .2273 | 99.0 | .0301 | |
| | (racemic) | .1498 | 99.0 | .0310 (.0306)[b] | .209[c] |

[a] Wt. per cent. ethanol. [b] Previously reported value (Ref. 1); see footnote c, Table I. [c] Previously reported value (Ref. 1); see footnote b, Table I.

of water to the methanol solvent and from the substitution of ethanol for methanol. It is evident that at least as far as non-ionic dibromides are concerned there is no doubt that the reaction is of the second order.

Two interesting comparisons can be drawn from the values of $k_2$ collected in Table IV. They are, first, at a given temperature the rates of reaction for all of the dibromides investigated are of the same order of magnitude, with the exception of ethylene bromide, which reacts much faster than the others, and, second, for a given compound the reaction rate is greater in the mixed solvent which has the higher molal fraction of water.

In Table V are given the values of the heats of activation $Q$, and the temperature coefficients for 10°, calculated according to the Arrhenius equation from the rate constants at 59.72 and 74.93°. It is interesting that the temperature coefficients of 1,2-dibromopropane and 1,2-dibromobutane are practically identical, a result not unexpected in view of their similarity in structure.

TABLE V

HEATS OF ACTIVATION AND TEMPERATURE COEFFICIENTS FOR REACTIONS OF DIBROMIDES WITH POTASSIUM IODIDE IN 99% METHANOL

| Dibromide | $k_2$ 59.72° | $k_2$ 74.93° | Heat of activation, cal. | Temperature coefficient for 10° 69.72°/59.72° | Temperature coefficient for 10° 74.93°/64.93° |
|---|---|---|---|---|---|
| $CH_2BrCH_2Br$ | 0.300 | 1.34 | 22700 | 2.73 | 2.64 |
| $CH_3CHBrCH_2Br$ | .0111 | 0.0582 | 25100 | 3.02 | 2.92 |
| $CH_3CH_2CHBrCH_2Br$ | .0148 | .0800 | 25500 | 3.09 | 2.98 |
| $CH_3CHBrCHBrCH_3$ (meso) | .00902 | .0563 | 27700 | 3.39 | 3.27 |
| $CH_3CHBrCHBrCH_3$ (racemic) | .00465 | .0304 | 28400 | 3.50 | 3.37 |

**Recalculation of van Duin's Results.**—The third order specific rate constants reported by van Duin[2,7] are not the same for different initial concentrations of potassium iodide. It may be readily seen from the results that second order constants would be in much better agreement. It suffices to say that the values which have been recalculated, while they do not agree as well as those given in Table IV, obviously indicate that van Duin was in error when he assumed that the rates were of the third order.

**Influence of Ionic Strength upon the Reaction Rates.**—The Brönsted theory[10] of the velocity of ionic reactions is well known and has been applied extensively. The effect of the ionic strength upon the classical second order specific rate constant is indicated by the relation $k_2 = k_0 10^{z_a z_b \sqrt{\mu}}$ which holds strictly only in dilute solution. However, even

[10] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); "Theory of the Velocity of Ionic Reactions" in the Columbia University Lectures, "Contemporary Developments in Chemistry," Columbia University Press, March, 1927; see also, Brönsted and Livingston, THIS JOURNAL, **49**, 435 (1927).

in the relatively concentrated solutions in which the rate measurements of the reaction between dibromides and iodide ion have all been made, the effects predicted by the Brönsted expression may be qualitatively demonstrated. Van Duin measured the rates of reaction of potassium and sodium iodide with dibromides capable of undergoing ionization and found an increase in the specific reaction rate with an increase in concentration of iodide ion or on the addition of various salts to the reaction mixture. Incidentally, the result was not ascribed to the Brönsted effect. The reaction of potassium and sodium iodide with a non-ionizable dibromide, namely, ethylene bromide, has been carried out in this work and in this case the rate was found to decrease only slightly on the addition of salts. Thus, in the case where both reactants are ionic and are of the same sign, the reaction rate increases with ionic strength, but where one of the reactants is electrically neutral, the ionic strength is without effect on the rates. The results are summarized in Table VI.

In addition it should be pointed out that the rates of reaction of dibromo acids with potassium iodide as reported in Table VI are not affected by altering the ionic strength of the solutions by changing the concentration of either the potassium iodide or the added hydrochloric acid. This is logical since the amount of hydrochloric acid present in these reactions should be sufficient to depress completely the dissociation of these weak organic acids so that in their reactions with iodide ion they conform to the case where one of the reactants is electrically neutral. It is not surprising, however, that the specific rate constant of 2,3-dibromopropanoic

TABLE VI

INFLUENCE OF IONIC STRENGTH ON THE REACTION RATES OF DIBROMIDES WITH POTASSIUM IODIDE

| | | Molal concn. KI | Added substance | Added substance | $\mu$ | $k_2 \times 10^3$ |
|---|---|---|---|---|---|---|
| | | 1.0 | ... | ... | 1.07 | 1.10 |
| A. | Ionized dibromide,[a] *p*-$NaSO_3C_6H_4$-$CHBrCHBrCOONa$, 0.025 *M* | 2.0 | ... | ... | 2.07 | 1.49 |
| | | 1.0 | 1.0 | KBr | 2.07 | 1.54 |
| | | 1.0 | 1.0 | KCl | 2.07 | 1.57 |
| | | 1.0 | 0.5 | $CaCl_2$ | 2.57 | 1.73 |
| B. | Un-ionized dibromide,[b] $CH_2Br$-$CH_2Br$, 0.022 *M* | 0.22 | ... | ... | 0.22 | 80.0 |
| | | .22 | 0.11 | KCl | .33 | 77.9 |
| | | .22 | .22 | KBr | .44 | 72.5 |
| C. | Undissociated dibromo acid,[c] $CH_2BrCHBrCOOH$, 0.025 *M* | .5 | .125 | HCl | .63 | 0.343 |
| | | 1.0 | .125 | HCl | 1.13 | .317 |
| | | 2.0 | .250 | HCl | 2.25 | .364 |
| | | 2.0 | .500 | HCl | 2.50 | .354 |

[a] These results were calculated from the data of van Duin (Ref. 2). Similar results may be calculated from his data for $CH_2BrCHBrCOONa$. [b] These results were obtained in this work: temp. 40°; solvent, 60% ethanol. [c] Also, recalculated from data of van Duin (Ref. 2). Other acids gave the same results.

acid under the various conditions tabulated (Table VI) differs from the rate[11] when there is no free hydrochloric acid present. In this last instance partial dissociation of the organic acid undoubtedly occurs.

## Summary

The reaction rates of potassium iodide with ethylene bromide and propylene bromide in methanol have been measured at 30, 60 and 75° and found to be of the second order. From the influence of iodine upon the rate it has been shown that in alcoholic solutions one mole of dibromide reacts with three moles of potassium iodide.

Previously reported second order constants for the reaction of the butylene bromides have been recalculated on this basis. From these rate constants, the heats of activation and temperature coefficients for ethylene bromide, propylene bromide and the three normal butylene bromides have been calculated.

Recalculation of van Duin's results show that the reactions of probably all dibromides with potassium iodide are second order and not third order as he claimed.

An increase in the ionic strength of the reaction medium by the addition of neutral salts slightly decreases the reaction rate of the non-ionic dibromides with iodide ion. On the other hand, under these conditions the reaction rate is appreciably increased in the case of ionized dibromides as the Brönsted theory demands.

[11] Ref. 2, p. 351: $k_3 = 0.123 \times 10^{-3}$, $k_2 = 0.246 \times 10^{-3}$.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# THE PHOTOCHEMICAL REACTION BETWEEN QUININE AND DICHROMIC ACID. I. QUANTUM YIELDS

BY GEORGE S. FORBES, LAWRENCE J. HEIDT AND CHARLES G. BOISSONAS[1]

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Earlier studies of this reaction[2,3,4] left unsolved a number of problems such as the relation of quantum yield to wave length, the consequences of light absorption by dichromic acid, and the details of the secondary processes. Bodenstein[5] and later Kistiakowsky[6] published critical discussions of these papers. Morton[7] has recently proposed a reaction mechanism in

[1] International Research Fellow, 1927–1928.

[2] Goldberg, *Z. physik. Chem.*, **41**, 1 (1902); *Z. Wiss. Phot.*, **4**, 56 (1906).

[3] Luther and Forbes, THIS JOURNAL, **31**, 770 (1909).

[4] Forbes, Woodhouse and Dean, *ibid.*, **45**, 1891 (1923).

[5] Bodenstein, *Z. physik. Chem.*, **85**, 329 (1913).

[6] Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, pp. 39–41.

[7] Morton, *J. Phys. Chem.*, **33**, 1135 (1929).

terms of his own observations upon the photochemical reaction between dichromic acid and alcohol. A reinvestigation of the subject using modern quantitative methods was begun, with Dr. Boissonas, in 1927–1928, and continued, with Dr. Heidt, in 1930–1931.

The apparatus and radiometric procedures were similar to those developed in this Laboratory by Villars,[8] P. A. Leighton[9] and W. G. Leighton.[10] Several variations require mention.

An improved mercury vapor lamp[11] was devised in which oscillations of mercury were controlled by plungers ground into arms open to the atmosphere. The monochromator had been constructed, in its original form, by Villars. A 60° glass prism, 115 × 115 × 115 × 80 mm. ($n_d$, 1.69), served to separate the radiations at 436, 405 and 366 mμ, while a fused quartz prism of equal size was used for the shorter wave lengths. When desired, thermopile and cell could be mounted side by side on a single carriage, propelled at right angles to the axis of the back lens. Fine adjustments were made by a screw of 0.5 mm. pitch having a reference mark on its milled head. Through the kind coöperation of Mr. F. P. Brackett, Jr., of this Laboratory a monochromator having crystal quartz optics and a zinc spark of high intensity and constancy[12] were available for the range 254 to 208 mμ.

A trapezoidal quartz cell (all seams fused) was thermostated on two sides at 5 ± 2° by circulating water. It had a tubulure and stirrer according to a design previously described.[10] The stirrer was provided with a mercury seal and was surmounted by a small windmill driven by a jet of compressed air. About three-quarters of our photolyses were run under carbon dioxide, the rest under air. No difference in quantum yield was noted, in agreement with the experience of Forbes, Woodhouse and Dean[4] and the statement of Weigert and Savenu[13] that the photolytic oxidation of quinine by oxygen is strongly inhibited by acid. A jet of carbon dioxide brought to 5° prevented dew formation on the front window. All the light from the exit slit of the monochromator (20 mm. × 1 to 2 mm.) fell upon this front window. The customary corrections for reflection were made and the emerging light, when not negligible, was properly estimated and deducted.

**Materials.**—Quinine bisulfate (Mallinckrodt U. S. P.) presumably contained less cinchonidine and other impurities than a normal sulfate. It was thrice recrystallized from 5% sulfuric acid between 60 and 0°, and the crystals centrifuged in the dark after each recrystallization. The last crop was dissolved in a large volume of water and precipitated as the base by a bare excess of dilute sodium hydroxide. The base was di-

[8] Villars, THIS JOURNAL, **49**, 326 (1927).

[9] P. A. Leighton, *ibid.*, **51**, 3549 (1929).

[10] W. G. Leighton, *ibid.*, **52**, 3139 (1930).

[11] Forbes and Heidt, *ibid.*, **53**, 4349 (1931).

[12] Forbes and Brackett, *ibid.*, **53**, 3973 (1931).

[13] Weigert and Savenu, *Nernst-Festschrift*, 464 (1912).

gested with several portions of boiling water, all lumps being carefully powdered. The final product was heated at 125° and kept in a vacuum desiccator over concentrated sulfuric acid. The melting point, 175°, agreed with that given in "International Critical Tables."[14] It left no residue on ignition, and the escaping gases gave no odor of sulfuric acid or reaction with blue litmus paper. A few photolyses run with U. S. P. quinine at 405 mμ gave quantum yields 20% higher than the material just described. Potassium dichromate (Baker's analyzed) was thrice recrystallized, with centrifuging in each case, and thoroughly dried. The other chemicals were of reagent quality. Conductivity water, for our stock solutions, was kindly furnished by Professor Grinnell Jones.

**Absorption Measurements.**—Villars[15] in this Laboratory proved that extinction coefficients can be accurately determined by integration of diverging light beams. For present purposes a simpler method based upon direct comparisons sufficed. Three cells were made of parallel fused quartz plates and divided into two compartments with carefully ground partitions of Pyrex glass. Their thicknesses, as measured with inside vernier calipers, averaged 3.02, 9.00 and 38.0 mm. The liquids came in contact with the de Khotinsky cement only in capillary spaces and only for short periods. One compartment contained the solution to be studied, the other water containing enough sulfuric acid to equalize the refractive indices. With the thermopile set behind the cell at the position of maximum deflection, the cell was slid back and forth perpendicular to the axis of the back lens of the monochromator, and readings taken behind the two compartments in alternation. The back focus of the lens being 410 mm., the divergence of the rays was small. After averaging the two sets of readings, the cell was well rinsed, dried and further readings taken with the solutions exchanged, so as to eliminate differences in the two compartments. Lambert's law was found to hold within 5% in all cases. The work was carried out at room temperature, after proof that $K_{0°} = K_{20°} = K_{30°}$. In all cases $K = -(\log_{10} L/L_0)/cd$, where $c$ is expressed in moles per liter and $d$ in cm. In general we restricted measurements to concentrations prevailing in actual photolyses.

Quinine bisulfate, $C_{20}H_{24}N_2O_2 \cdot H_2SO_4$ = Q, does not follow Beer's law and $K_q$ varies with acidity as well. Figure 1 shows log $K_q$, in 1.7 molar sulfuric acid, from 405 to 208 mμ. Data graphed as solid circles were determined as described above. Mr. Brackett kindly made the measurements at 208 mμ. Open circles were located by a null photographic method, using a comparison quartz spectrograph after Judd Lewis,[16] kindly put at our disposal by Dr. F. L. Gates.[17] Squares represent data from the "International Critical Tables,"[18] corrected for a difference in $[H_2SO_4]$. The close agreement of data obtained by several methods is reassuring. Figure 2 shows how $K_q$ varies at 405 mμ and at 366 mμ with changing acidity. The striking differences in the shapes of the curves suggest that more than one absorption mechanism is involved. This possibility is further considered below.

The solution termed dichromic acid contains various ions and molecules,

[14] "International Critical Tables," Vol. I, p. 266.

[15] Villars, *J. Opt. Soc. Am.*, **14**, 29 (1927).

[16] Judd Lewis, *J. Chem. Soc.*, **115**, 312 (1919).

[17] Gates, *J. Gen. Physiol.*, **14**, 37 (1930).

[18] "International Critical Tables," Vol. V, p. 371.

the concentrations of which vary with acidity as well as with total concentration. Unit concentration assumes 104 g. of chromium per liter. The extinction coefficient, $K_c$, at fixed wave length, is depicted by a set of plane curves. Figure 3 shows the effect of changing the acidity at each of four wave lengths, $[H_2Cr_2O_7]$ being fixed at 0.00042. Circles give our data by thermopile. Crosses in circles are after Viterbi and Krausz,[19] and crosses are after Hantzsch and Clark,[20] for solutions not acidified. In Fig. 10, $K_c$ is given for a solution in which $[H_2Cr_2O_7] = 0.00016$ in 0.8 $M$ $H_2SO_4$. The measurements at 208 m$\mu$ were made by

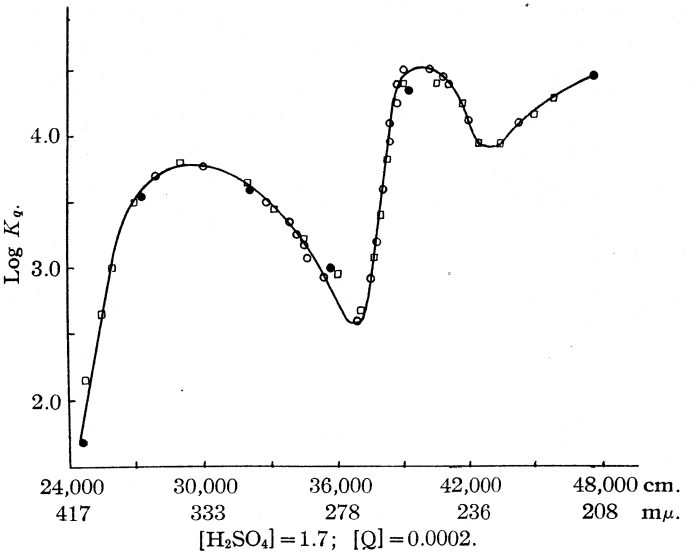



Fig. 1.—□, Values from "I. C. Tables," Vol. V; ○, values by null photographic method; ●, values by spectroradiometer with thermopile.

Mr. Brackett. We refrain from presenting all our data. It was found that $K_c$ increases 15% at 405 m$\mu$, and 20% at 366 m$\mu$, in passing from 0.0001 to 0.001 $M$, the sulfuric acid being 0.125 $M$ in all cases. The rate of increase in $K_c$ falls off slowly as $[H_2Cr_2O_7]$ increases. Measurements on samples of dichromic acid reduced by sulfite showed that $K_{Cr^{+++}}$ was negligible in comparison with $K_c$ at 405, 366, 313 and 280 m$\mu$, so no correction for inner filter effect of chromic ion formed by reduction was made.

Radiometric procedures described in other papers[8,9,10] from this Laboratory were simplified after proof, by Mr. Brackett,[12] that $E$, the total energy flux of the beam diverging from the exit slit of the monochromator, as determined by integration over the entire width of the beam, was closely

[19] Viterbi and Krausz, *Gazz. chim. ital.*, **57**, 690 (1927).

[20] Hantzsch and Clark, *Z. physik. Chem.*, **63**, 367 (1908).

proportional to $D$, the maximum galvanometer deflection obtainable during the excursion, provided that no part of the optical train was displaced. Before every other run, $E/D$ was redetermined as above. During runs the maximum deflection $D_n$ was frequently redetermined, whereupon $E_n = D_n \times E/D$. Fluctuations in $E_n$ were thus taken into account. From the various values of $D_n$ and the time, the total quanta incident upon the front window of the cell was built up by summation or by graphical integration. Suitable corrections were always made for reflection and

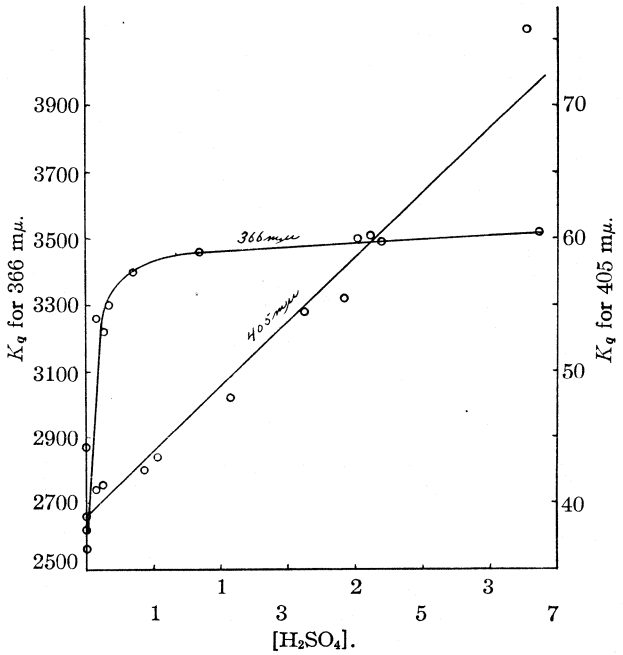



Fig. 2.—Upper scale for 366 mμ; lower scale for 405 mμ; λ 405 mμ, [Q], 0.0080; λ 366 mμ, [Q], 0.0004.

absorption at the front window, and whenever absorption was incomplete, reflection and transmission at the rear window were estimated as well. The absence of infra-red light was demonstrated, at each wave length, by the use of electric smoke glass. The sensitivity of the thermopile–galvanometer system was rechecked daily to eliminate a number of influences not easily definable. About once in six weeks, absolute calibrations were made against radiation standard C 69 of the Bureau of Standards according to accompanying directions.

**Analyses** were carried out electrometrically, using weight burets. A weighed sample of solution after photolysis was in each case compared with a sample of the original solution preserved meanwhile at the same tem-

perature in the dark. In the earlier work, following a suggestion by Dr. J. G. Aston, the reducing agent was potassium ferrocyanide, 0.0007 *M*. The e. m. f. against a calomel electrode was directly measured, and plots for the two samples were made side by side. The end-point of the photolyzed sample was recognized by a sharp divergence of its plot from the other. In the later work the method of Forbes and Bartlett[21] was followed, using, however, a half-cell of mercury, mercurous sulfate and sulfuric acid. Mohr's salt (0.0005 to 0.01 *N*) made up from clear green crystals was added

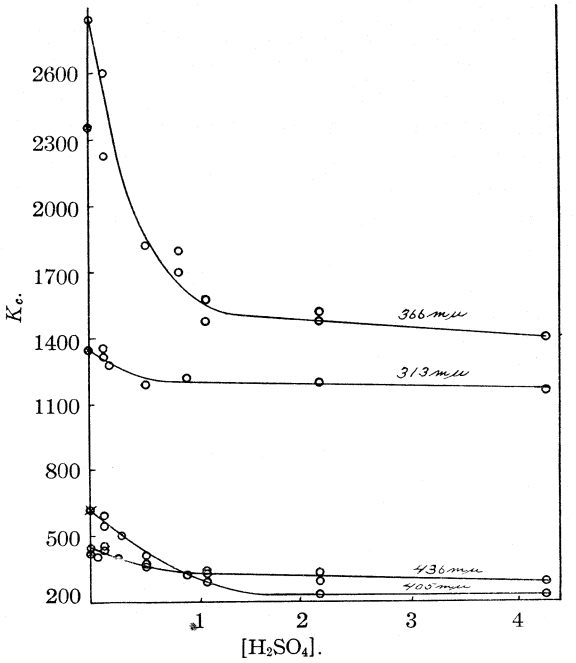



Fig. 3.—[$K_2Cr_2O_7$], 0.00042; ×, Hantzsch and Clark; ⊗, Viterbi and Krausz.

until the anomalous rise in oxidizing potential gave way to a precipitous decline at the end-point. The reducing solution, in each method, was frequently compared with standard dichromate, and the true factors at other times interpolated. Changes in titer during photolysis were calculated to oxygen atoms lost by dichromic acid. Reduction of dichromic acid varied between $10^{-7}$ and $10^{-5}$ mole, usually about 5% of the initial amount but as much as 30% in a few cases. As the end-point in many cases could be fixed only within 10% of the dichromic acid photolyzed, the analysis was distinctly less accurate than the radiometric work, and much attention was given to small improvements in the former.

[21] Forbes and Bartlett, THIS JOURNAL, **35**, 1527 (1913).

**The dark reaction** at 5 ± 2° was proved to be less than the analytical errors unless $[Q][H_2Cr_2O_7][H_2SO_4] > 2.5 \times 10^{-6}$ and $[H_2SO_4] > 1$. The correction, which never exceeded two-tenths of the light reaction, was made wherever desirable. It was proved, in separate experiments, that the oxidation products of quinine absorb light to about the same extent as the original quinine. Special experiments on solutions previously exposed to light indicated that the quantum yield, $\phi$, increases slowly as the reaction continues, which suggests that the oxidation products of quinine are more reactive than quinine itself. We are now photolyzing various quinine derivatives in the hope of correlating $\phi$ with structural peculiarities.

Gross quantum yields, $\phi$, signify total oxygen atoms transferred from dichromic acid to quinine divided by total quanta absorbed within the solution. The quanta absorbed by water could always be neglected. The net quantum yield, $\phi_q$, is referred to quanta absorbed by quinine alone. These were calculated by the use of formulas of Luther and Weigert,[22] introducing the values of $K_q$ and $K_c$ measured separately at the same concentration and acidity. The additivity of absorptions presupposed by these formulas was proved by special experiments at widely varied concentrations and wave lengths. Thus it appears that the present system is not analogous to uranyl oxalate, where the photolysis occurs within a stable complex having an absorption very different from that calculated by simple addition.

To conserve space we present most of our bulky data on two hundred photolyses by graphs embodying the end results. Each point on a graph represents the average of at least two, usually three and sometimes four, photolyses. Single values of $\phi$ at the worst are subject to an error of about twenty per cent., usually not more than ten per cent.

Experiments carried out at different light intensities are comparable only after correction for deviation from the reciprocity law. Figure 4, at 366, 313 and 280 m$\mu$, shows that $\phi$ and $\phi_q$ decrease as $E$ increases. In a later paper the complicated kinetic phenomena underlying this effect will be analyzed. Unfortunately, still higher light intensities were not available, and the photolytic rate at still lower light intensities would have been too small to measure accurately. The values of $\phi_q$ as given correspond to the actual $\phi_q$ in a thin layer about one-third of the distance between the front window and a point where some 99% of the light has been absorbed. Rigorous mathematical treatment would require an integration over the entire absorbing layer[23,24] in which the energy flux $E_d$ varies with $d$, the depth of solution already traversed, and $\phi_q$ in turn varies with $E_d$.

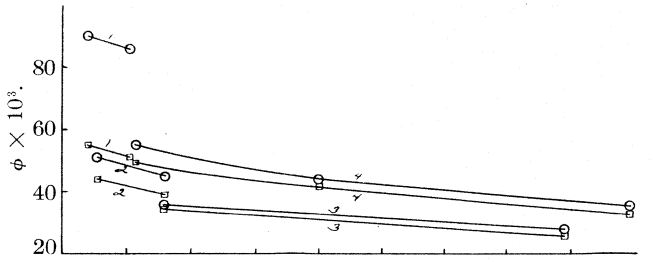
**Activation.**—Three apparently perfect experiments in blue light,

[22] Luther and Weigert, *Z. physik. Chem.*, **53**, 408 (1905).

[23] Forbes, *J. Phys. Chem.*, **32**, 488 (1928).

[24] Allmand, *J. Chem. Soc.*, 1557 (1929).

436 mμ, produced no detectable photolysis in a solution in which $[H_2Cr_2O_7]$ = 0.02, $[H_2SO_4]$ = 0.8 and [Q] = 0.2, all in spite of strong absorption by dichromic acid. The latter when activated by such quanta readily attacks alcohol[7,25,26] and other compounds, but it must attack non-activated quinine with negligible velocity. This conclusion is identical with that of Luther and Forbes.[3] As it is impracticable to work with a solution of such thickness and concentration that quinine absorbs a significant fraction of incident light at 436 mμ, it must remain an open question whether quinine can be activated by such quanta[27]. In Fig. 5, $\phi$ and $\phi_q$ are plotted against [Q] at each of six wave lengths, $[H_2Cr_2O_7]$ and $[H_2SO_4]$




○, $\phi_q$. Quanta × 2 × $10^{-17}$ absorbed by quinine/min. per cc.;
□, $\phi$.

Fig. 4.—Temp., 25°.

| Number | λ in mμ | $[K_2Cr_2O_7]$ | [Q] | $[H_2SO_4]$ |
|---|---|---|---|---|
| 1 | 280 | 0.00016 | 0.001 | 0.8 |
| 2 | 280 | 0.00004 | 0.001 | 0.8 |
| 3 | 313 | 0.00004 | 0.00025 | 0.8 |
| 4 | 366 | 0.00004 | 0.00025 | 0.8 |

being held constant at 0.00016 and 0.8, respectively. The lines for $\phi_q$ have a negative slope, partly because, as [Q] increases, it absorbs a greater fraction of the total energy flux, which was approximately the same in all cases. The deviations from the reciprocity law have been shown in Fig. 4, where total light intensity was varied while keeping constant the fraction absorbed by quinine. The indicated corrections when applied to the points in Fig. 5 would change somewhat the slopes of the curves. Obviously $\phi_q$ is independent of the fraction of the total energy flux absorbed by quinine, provided only that this flux and $[H_2Cr_2O_7]$ and $[H_2SO_4]$ remain constant. Identical conclusions follow from other sets of experiments carried out in other (constant) concentrations of dichromic acid. On the other hand, the net quantum yield, $\phi_c$, referred to quanta absorbed by dichromic acid in our experi-

[25] Bowen and Bunn, *J. Chem. Soc.*, 2353 (1927).

[26] Bunn and Yarnold, *ibid.*, 1648 (1929).

[27] We shall show in a later paper that when quinine is replaced by cinchonine, the absorption curve of which resembles that of quinine shifted some 2000 cm.$^{-1}$ toward the ultraviolet, no photolysis occurs at 405 mμ, but at 366 mμ, $\phi$ for cinchonine approximates that for quinine at 450 mμ under conditions otherwise identical.

ments assumed values from 0.007 to 2000, when the fraction of the total energy flux which was absorbed by dichromic acid was widely varied. The above facts may be interpreted through the hypothesis that the reaction between activated dichromic acid and non-activated quinine is slow in comparison with that between activated quinine and dichromic acid whether activated or not. The conclusion of Luther and Forbes[3] that photolysis at 405 and 366 m$\mu$ depends upon activation of quinine alone when $[H_2SO_4] > 1$, thus receives strong support. On the other hand, it has long been known that dichromic acid, at shorter wave lengths, is directly photolyzed to

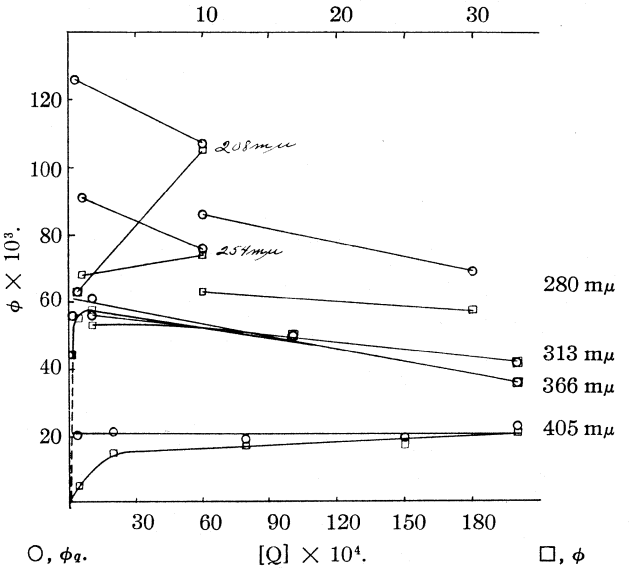



Fig. 5.—Lower scale for 405, 366 and 313 m$\mu$; temp., 5°; upper scale for 280, 254 and 208 m$\mu$; temp., 25°; $[H_2SO_4]$, 0.8; $[K_2Cr_2O_7]$, 0.00016.

chromic ion and oxygen. We irradiated dichromic acid, without quinine, and noted no photolysis at wave lengths exceeding 280 m$\mu$. At 254 m$\mu$, $\phi = \phi_c = 0.006$, and at 208 m$\mu$, $\phi = \phi_c = 0.015$. At 254 and at 208 m$\mu$, $\phi_q$ is therefore subject to a correction in consequence of this side reaction. Of course dichromic acid activated by such large quanta may oxidize non-activated quinine directly instead of evolving oxygen. Such a situation, assuming two activated components, was outlined by Forbes, Woodhouse and Dean.[4] We are continuing measurements at 208 m$\mu$ to clarify this aspect of the problem.

Gross and net quantum yields alike increase with increasing acidity as shown in Figs. 6, 7, 8 and 9 and Table I. The acidity in the more acid solutions was not recalculated to hydrogen-ion activity. Separate experiments

showed that potassium and sodium ions had a negligible effect upon quantum yields. Experiments at very low acidities must be made unduly long owing to minimal quantum yields; also chromate ion is precipitated by quinine and by chromic ion formed by reduction unless all concentrations are extremely

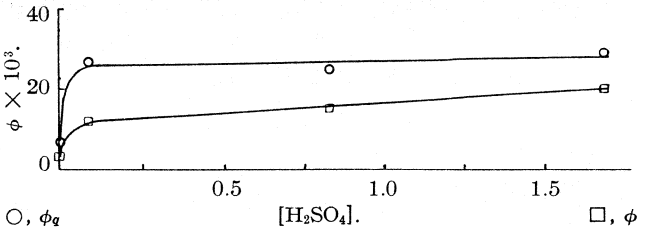



Fig. 6.—λ, 405 mμ; [$K_2Cr_2O_7$], 0.00016; [Q], 0.002; temp., 23°.

small. Any turbidity, of course, would bar interpretation of results. It was therefore inadvisable to follow Plotnikow's[28] suggestion that the reaction be followed in neutral solution. We are, however, making experiments at low acidities and varying quinine concentrations to test Morton's[7]

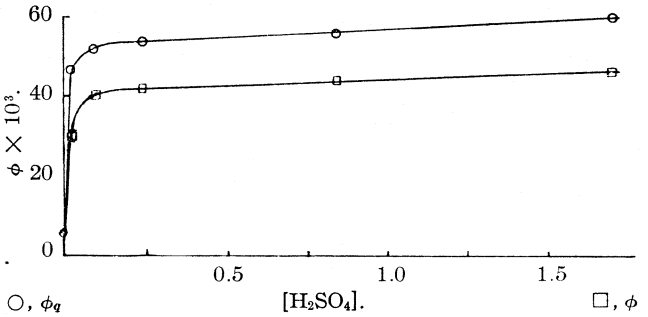



Fig. 7.—λ, 366 mμ; [$K_2Cr_2O_7$], 0.00016; [Q], 0.00025; temp., 5°.

Table 1. Temp., 5°.

| λ, in mμ | [$K_2Cr_2O_7$] | [Q] | [$H_2SO_4$] | $P_H$ | Buffer | ø | $ø_q$ |
|---|---|---|---|---|---|---|---|
| 366 | 0.00016 | 0.00025 | 0.0 | 2 | $NaHSO_4$ | 0.030 | 0.047 |
| 366 | 0.00016 | 0.00025 | 0.0 | 6 | $KH_2PO_4$+ $Na_2HPO_4$ | 0.000 | 0.000 |
| 366 | 0.00008 | 0.00025 | 0.2 | | | 0.041 | 0.048 |
| 366 | 0.00008 | 0.00025 | 0.4 | | | 0.047 | 0.052 |
| 366 | 0.00008 | 0.00025 | 0.8 | | | 0.041 | 0.048 |

hypothesis that activation of dichromic acid increases with increasing [$H_2SO_4$] up to 0.37 molar, where it reaches a maximum value incapable of further increase through absorption of light quanta.

[28] Plotnikow, "Lehrbuch der Photochemie," Walter de Gruyter and Co., Berlin and Leipzig, 1920, p. 215.

Inspection of Figs. 1, 2 and 3 and of Figs. 6, 7, 8 and 9 shows that extinction coefficients and quantum yields do not, in general, change in corresponding fashion when acidity is varied. The increase in photolytic efficiency due to increase in acidity might then better be discussed upon the basis of other considerations. These will be presented in a subsequent paper.

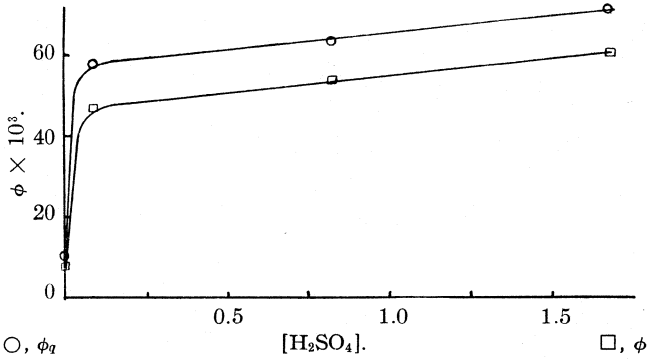



Fig. 8.—λ, 313 mμ; [$K_2Cr_2O_7$], 0.00016; [Q], 0.00025; temp., 23°.

Quantum yields at various wave lengths, roughly corrected to a basis of equal average light intensities expressed as quanta absorbed by quinine, appear in Fig. 10. All points at 254 and 208 mμ have been subjected also to small corrections for direct photolysis of potassium dichromate. It is

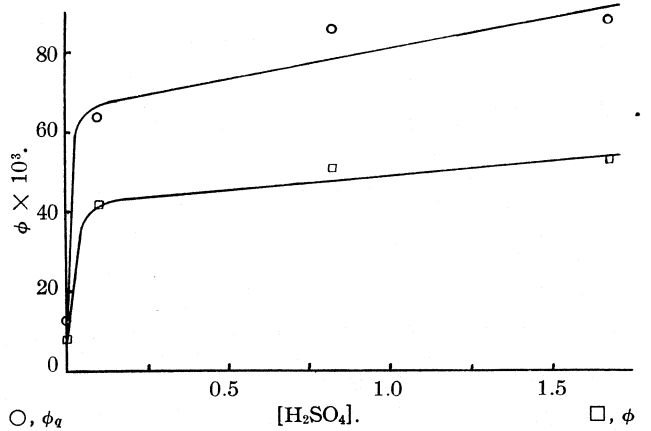



Fig. 9.—λ, 280 mμ; [$K_2Cr_2O_7$], 0.00016; [Q], 0.001; temp., 23°.

seen that $\phi_q$ is smallest at 405 mμ, rises sharply to 366 mμ, is unchanged at 313 mμ, then climbs steeply to 208 mμ. The conclusion of Luther and Forbes[3] that photochemical efficiency at 405 mμ is nearly four times as great as at 366 mμ is in error because of their assumption, since disproved

by Winther,[29] that spectral energy distribution of an uviol lamp can be taken without serious error as equal to that of a quartz lamp. The absorption curves of quinine and of dichromic acid are inserted for comparison and it appears that the plot of $K_c$ follows that of $\phi_q$ much more closely than the plot of $K_q$. This coincidence, however, does not necessarily imply a causal relation. Between 405 and 366 m$\mu$ a new type of absorption mechanism for quinine seems to assert itself as suggested from a comparison of curves correlating $K_q$ with $[H_2SO_4]$ at 405 and 366 m$\mu$. Beyond 313 m$\mu$ the apparent quantum yield rises with increasing frequency except for a second dip at 254 m$\mu$.

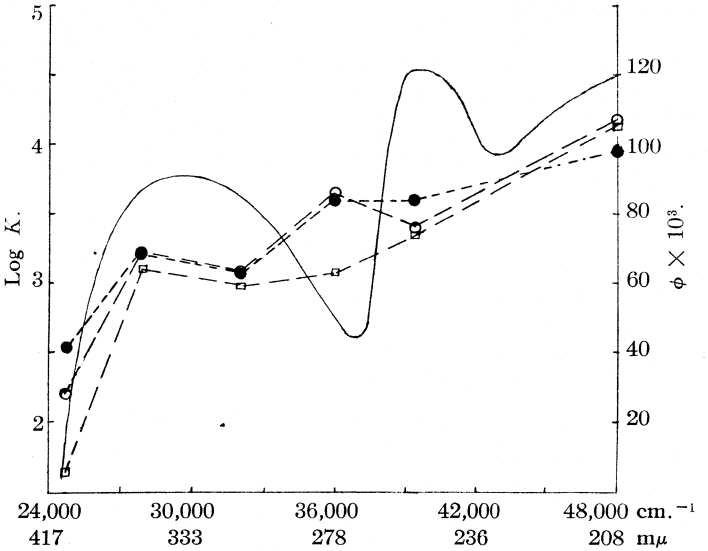



Fig. 10.—Temp., 26°; $[K_2Cr_2O_7]$, 0.00016; [Q], 0.001; $[H_2SO_4]$, 0.8; ○, $\phi_q$; □, $\phi$; ●, log $K$ for $K_2Cr_2O_7$ in 0.8 $M$ $H_2SO_4$; ——, log $K$ for quinine in 0.8 $M$ $H_2SO_4$.

Fifty experiments, to be described in a later paper, fixed $[\phi_q]_T + 10/[\phi_q]_T$ between 2 and 29° at 1.12 ± 0.03. Tentative calculations (L. J. H.) show that a bimolecular collision number in aqueous solution has the same coefficient. This agreement would be expected if the secondary act involved reduction of dichromic acid, following a bimolecular collision with activated quinine, and requiring no additional activation energy.

A superficial examination of the structure of the quinine molecule shows that it consists of a quinoline group connected through a secondary hydroxyl to a saturated ring structure. The absorption curve is mainly conditioned by the former group as pointed out by Dobbie and Lauder,[30]

[29] Winther, *Z. Elektrochem.*, **19**, 389 (1913).

[30] Dobbie and Lauder, *J. Chem. Soc.*, **99**, 1254 (1911).

and as further demonstrated by comparing the absorption curve of quinine with those of numerous quinoline derivatives as given in "International Critical Tables."[31] Rabe,[32] however, has demonstrated that in the purely thermal reaction between quinine and dichromic acid it is the secondary hydroxyl, not the quinoline group, that is first attacked, since the initial oxidation product is the corresponding ketone. We have examined the absorption coefficients of a number of secondary alcohols, but have found them negligible in comparison with those of compounds containing the quinoline group except perhaps at 208 mμ. To explain the apparent anomaly it might be assumed that vibrational energy transmitted through the activated quinoline group to the secondary hydroxyl can activate the latter. The increase in $\phi_q$ in passing from 313 to 208 mμ might possibly result from the increasing excess of vibrational energy set up in the quinoline group by the ever-increasing quanta. Such an hypothesis does not explain the dips of the curve near absorption maxima. We are now investigating various quinine derivatives to test these tentative suggestions.

## Summary

The photochemical reaction between quinine and dichromic acid has been reinvestigated quantitatively at each of seven wave lengths from 436 to 208 mμ with analytical and radiometric precautions sufficient to establish quantum yields within 10%.

Extinction coefficients of quinine and dichromic acid were measured at each of these wave lengths, and over a wide range of concentrations and acidities using various apparatus and methods. Quantum yields change similarly with $[H_2SO_4]$ for 405, 366, 313 and 280 mμ and cannot be correlated with changes in $K_q$ or $K_c$ with $[H_2SO_4]$. Extinction coefficients proved to be additive within the limit of error; it is improbable, therefore, that quinine and dichromic acid form a stable complex analogous to that of uranyl oxalate.

The hypothesis that activation of quinine is the decisive factor in the photolysis is strongly supported by the outcome of about two hundred photolyses. Apparently irradiation of dichromic acid does not increase its tendency to react with non-activated quinine except perhaps at wave lengths shorter than 280 mμ. Further experiments in this spectral region are in progress.

Tentative calculations indicate that the reaction's temperature coefficient, $1.12 \pm 0.03$, equals that of a bimolecular collision number in aqueous solution, presumably involving dichromic acid and activated quinine, and resulting in reduction of the former without additional activation energy.

A plausible scheme of reaction mechanism begins with the capture of

[31] "International Critical Tables," Vol. V, pp. 363–372.

[32] Rabe, *Ann.*, **365**, 353 (1909).

a quantum by the quinoline group of the quinine molecule. Vibrational energy, transferred to the secondary hydroxyl group adjacent, may increase the reactivity of the latter.

Parallel experiments with quinine derivatives are being made. Temperature coefficients and the effects of variable dichromate concentrations, especially at low acidities, are being investigated.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE LABORATORY OF PLANT NUTRITION OF THE UNIVERSITY OF CALIFORNIA]

# ATTEMPTED PHOTOSYNTHESIS OF CARBOHYDRATES IN VITRO WITH VISIBLE LIGHT

BY F. PAUL ZSCHEILE, JR.

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The appearance in 1927 of three papers[1] by E. C. C. Baly and others on the "Photosynthesis of Naturally Occurring Compounds" was of very great interest to those concerned with photosynthesis as it occurs in the living green plant. Particular importance was attached to the second paper of this series, in which was described a method for the photosynthesis of carbohydrates from carbonic acid by means of visible light and colored solid catalysts. Forty futile attempts were made by the writer to repeat the experiments of Baly with visible light and nickel and cobalt carbonates as catalysts, with hopes of extending these experiments. Special precautions were taken to eliminate contamination of the photosynthetic system by impurities from various sources, precautions which were more rigorous than those described by Baly in the second paper mentioned above.

In paper II, Baly describes a precipitation method for preparation of carbonates of nickel and cobalt by adding cold solutions of nickel or cobalt nitrate and of potassium carbonate together and washing the precipitate with hot water to remove all foreign ions and alkali. The precipitate is then dried at 100° and powdered. The powder requires activation before introduction into the photosynthetic chamber, this activation being accomplished either by heating at 120–140° for thirty minutes or by exposing the powder to ultraviolet light for thirty minutes. The powder is then placed in conductivity water through which a stream of carbon dioxide is bubbled, this system being illuminated by visible light from electric lamps. After two hours, the mixture is filtered and the filtrate evaporated. The final residue is extracted with methanol, which removes the photosynthesized substance. This substance is said to reduce Benedict's solution, as well as to give other tests for carbohydrates. Baly's directions are rather incomplete as to details but they were followed as closely as possible, with some refinements, in the experiments described below.

An effort was made to exclude all sources of contamination, both organic and in-

[1] E. C. C. Baly, J. B. Davies, M. R. Johnson and H. Shanassy, *Proc. Roy. Soc.* (London), **A116**, 197 (1927); E. C. C. Baly, W. E. Stephen and N. R. Hood, *ibid.*, **A116**, 212 (1927); E. C. C. Baly and J. B. Davies, *ibid.*, **A116**, 219 (1927).

organic, in the preparation of the materials to be used in the system. All the water was redistilled in an all-glass Pyrex still, being collected and kept in Pyrex glass-stoppered flasks or flasks whose corks were covered with tin foil. In many cases the water was saturated previous to the experiment with the bicarbonate of the metal involved by bubbling carbon dioxide from the purification train through the water and carbonate mixtures for one and a half to two hours and filtering off excess carbonate. Using such water, the surface of the activated catalyst should not dissolve off immediately when placed in the illumination chambers. The resulting solution, tested with brom thymol blue, had a $P_H$ of 6.6–6.9 in the case of nickel carbonate and 6.2–6.3 with cobalt carbonate, so that alkalinity, warned against by Baly, was avoided.

The carbon dioxide was supplied from a tank, having been originally made by heating calcium carbonate. However, such carbon dioxide contains impurities, as is shown by the yellow oil which is left on sublimation of solid carbon dioxide. To purify it, the carbon dioxide was led from the tank through a lead tube, soldered to the valve outlet, into a Pyrex combustion tube which lay in a gas furnace. The juncture between the combustion tube and the lead tube was sealed with Insalute cement. This combustion tube, of 2.5 cm. external diameter, was heated to red heat. The entering gas first passed through a 60-cm. column of cupric oxide granules, and then over a reduced copper spiral 13 cm. long. After issuing from the combustion tube, it was washed through about 300 cc. of water and then passed through a cooling coil, made of Pyrex tubing of 0.9 cm. external diameter, containing 15 coils, each having a 4 cm. internal diameter. The object of this cooling was to freeze out any impurities that would not be volatile at the temperature of solid carbon dioxide, with which the cooling coil was surrounded. From this coil, the carbon dioxide entered the illuminated reaction vessels. Three Pyrex tubes were used as reaction chambers. Their wall thickness was 2 mm., their inside diameter 2.6 cm. and their illuminated length 26 cm. The three tubes presented an area of 203 sq. cm. to the source of light, and had a total volume of 450 cc. They were provided with ground-glass stoppers. The carbon dioxide bubbled through each tube in succession, at the rate of 12 liters per hour, the bubbles keeping the catalyst powder continually stirred and in suspension. Throughout the entire apparatus, there were no corks or rubber tubing. From the time the carbon dioxide entered the hot combustion tube until it had passed into the air from the last of the illuminated chambers, it was in an all-glass enclosing system. Before each experiment, the glass outlet from the purification train was sealed to the glass tube which entered the reaction vessels.

A number of catalysts were used, chiefly the carbonates of nickel and cobalt. The catalysts most used were prepared by adding one mole of the nitrate of nickel or cobalt (Baker's C. P.) dissolved in 150 cc. of water to one mole of sodium carbonate in 450 cc. of water, each solution having first been filtered. The precipitate was added to 550 cc. of water, heated to boiling and centrifuged, the liquid being discarded and the precipitate washed again in the same manner. The nickel carbonate was washed nineteen times and the cobalt carbonate fourteen times. They then contained no nitrate, as shown by the ferrous sulfate ring test, and less than 0.0007% of chloride and 0.0002% of sulfate as shown by tests with silver nitrate and barium chloride. After drying for two and a half hours at 100°, the carbonates were ground to a fine powder in an agate mortar. Baker's C. P. nickel carbonate and cobalt carbonate were washed twelve times with boiling water, 100 g. to 550 cc. of water, which was removed by centrifugation. They then contained less than 0.0007% of chloride and 0.0002% of sulfate, which were the limits of the tests used. Some other catalysts tried were: $Co_3O_4$ deposited on pumice; charcoal made from sucrose; the oxides of nickel and cobalt made by heating the carbonates; ferric oxide dialyzed with collodion; ferric hydroxide made by hydrolysis of ferric chloride, and dialysis with collodion; and colloidal cupric oxide and platinum, made by underwater arcs.

The catalysts were activated chiefly by exposure to the radiation from an air-cooled, Hanovia, mercury arc lamp at a distance of 15 cm., the powder being spread on a 25-cm. watch glass and stirred every five minutes during the activation period of thirty minutes. Heating to 120–130° in an oven was also tried as a means of activation. The time between activation of the powder and exposure to carbon dioxide and light was from eight to ten minutes; 1.5 g. of powder was used for each illuminated tube, or 4.5 g. for 450 cc. of water. Most of the exposures to light lasted for one and a half hours, but some experiments lasted two, three and six and a half hours.

Various light intensities were used, a conical reflector being placed behind the Mazda lights. The wattages of the lamps were 100, 300, 500 and 1000, the 100 and 300 watt lamps being used most. The distance of the filament from the illumination chambers was from 7.6 to 15 cm. In two experiments with nickel and cobalt carbonates, bright sunlight was used as a light source, carbon dioxide being taken directly from the tank through a rubber hose in these cases only.

In most of the experiments a stream of air from an electric fan was kept continually flowing over the illumination chambers to prevent excessive heating from the light source. The temperatures of the suspension in the tube at the end of the illumination period with various light intensities were as follows: 100 watt, 25°; 300 watt, 33°; 500 watt, 36°; 1000 watt, 52°; 300 watt, no fan, 57°; and sunlight, 35°.

After the illumination period, the aqueous suspensions from all these tubes were filtered and the filtrate evaporated to 10 cc. on the steam-bath. The carbonate was filtered off and the filtrate treated with a few drops of hydrochloric acid, and heated on a water-bath for one hour to hydrolyze any complex carbohydrates that might have been synthesized. After neutralization with sodium carbonate, the solution was evaporated to 2 cc., added to 5 cc. of Benedict's solution and heated to boiling. The solution was then centrifuged for ten minutes to deposit any cuprous oxide that might not have been visible without centrifugation. One milligram of glucose gives a quite large precipitate of cuprous oxide under these conditions, and probably no difficulty would be found in detecting 0.1 of a milligram of glucose by this method.

The carbon dioxide was, in several experiments, bubbled through 300 cc. of sodium bicarbonate solution mixed with glass beads, after coming from the combustion tube. The gas issuing from such a system in fifty minutes gave 19 cc. of gas which was not absorbed by a solution of sodium hydroxide, showing the presence of a gaseous impurity. Other experiments were run in which the tank carbon dioxide and the combustion furnace were not used, but carbon dioxide was obtained by heating pure sodium bicarbonate. Here, again, all-glass connections were used and the gas was passed through a solution of sodium bicarbonate and the cooling coil before entering the illumination chamber.

Comparing, as nearly as possible, the above conditions with the suspension's surface exposed to light and amount of catalyst used in Baly's experiments, a yield of about 10 mg. of carbohydrates should have been obtained. The test used would detect one hundredth of this amount. At the time this work was done, the paper[2] on the temperature coefficient of the reaction had not appeared. Baly and Hood describe a maximum yield at 31°. The work described above for 100 and 300 watt lamps should have given satisfactory results so far as temperature is concerned.

However, in no case was a cuprous oxide precipitate found in Benedict's test, all the experiments giving totally negative results. In such work there are many sources of error. The writer does not consider that Baly has necessarily removed all sources of organic impurities, since he used carbon dioxide from a cylinder without purification. His control experi-

[2] E. C. C. Baly and N. R. Hood, *Proc. Roy. Soc.* (London), **A122,** 393 (1929).

ments do not necessarily prove the total absence of organic impurities in his system, since it is possible that his carbon dioxide might have contained an organic impurity which required all of the conditions of his successful experiments for its transformation to an organic substance giving the tests described above. Such an impurity might not have been detected in his control experiments.

The recent papers[3] of Rao and Dhar report success in the synthesis of carbohydrates from carbon dioxide by means of the carbonates of nickel and cobalt in sunlight. The data presented are not quantitative. It is interesting that they obtained carbohydrates in 2% sodium bicarbonate solution, while Baly reported that all traces of alkali must be removed from the catalyst in order to obtain positive results.

Emerson,[4] using a carbonate of nickel prepared electrolytically and exposed to visible light before use, was not able to detect any production of oxygen as a result of illuminating the system, nor did he find that the absorption of carbon dioxide (found to be reversible at any point) was changed in rate by illumination. He also found no carbohydrate by the test of visible charring.

In paper IV, and in *Nature*,[5] Baly describes other methods of preparation of different and more active catalysts. It is quite possible that the method of catalyst preparation used by the writer is not exactly the same as Baly's, but so far as Baly's published directions permit, the author has been unable to reproduce, with positive results, any of Baly's experiments with visible light, using nickel or cobalt carbonates prepared by the precipitation method. In the opinion of the writer, none of these papers describe in sufficient detail the methods used, so that Baly's experiments might readily be successfully repeated from his directions.

The writer wishes to thank Professor D. R. Hoagland for certain suggestions received during the progress of the work.

## Summary

1. Attempts were made to repeat the experiments reported by Baly in 1927, in which he claims to have synthesized carbohydrates *in vitro* from carbon dioxide and water, using the carbonates of nickel and cobalt as catalysts, suspended in water saturated with carbon dioxide and illuminated by visible light.

2. Special precautions were taken to purify the carbon dioxide used and Benedict's test was used for the detection of carbohydrates.

3. The results were all absolutely negative.

CHICAGO, ILLINOIS

[3] G. G. Rao and N. R. Dhar, *J. Phys. Chem.*, **35**, 1418, 1424 (1931).

[4] R. Emerson, *J. Gen. Physiol.*, **13**, 163 (1929).

[5] E. C. C. Baly, *Nature*, **126**, No. 3182, 666 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

# THE REDUCTION OF NITRITES TO HYDROXYLAMINE BY SULFITES

BY G. K. ROLLEFSON AND C. F. OLDERSHAW

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A common method for the preparation of hydroxylamine has been to pass sulfur dioxide gas slowly into a cold mixture of sodium nitrite and sodium carbonate in water until the solution is just acid to litmus.[1] The hydroxylamine disulfonate ion formed by this process was hydrolyzed by heating the solution, which was then evaporated to dryness and the hydroxylamine extracted as either the sulfate or chloride. The following equations represent the two steps

$$NO_2^- + 2HSO_3^- + H^+ = HON(SO_3)_2^{=} + H_2O$$
$$HON(SO_3)_2^{=} + 2H_2O = HONH_3^+ + 2SO_4^{=} + H^+$$

The yields obtained by following this procedure are usually less than 50% of the theoretical. We have found it possible to obtain a much higher yield by modifying the above procedure so as to eliminate some of the possibilities for side reactions.

The factors to be considered in selecting the optimum conditions for this preparation are: the effect of hydrogen-ion concentration, the effect of temperature, and the effect of excess of either nitrite or sulfite. As a result of a series of tests at various concentrations of hydrogen ion we can say that the rate of formation of the hydroxylamine disulfonate ion becomes very slow if the $H^+$ falls below $5 \times 10^{-6}$ but proceeds readily at concentrations between $2 \times 10^{-5}$ and $5 \times 10^{-5}$. At higher concentrations, particularly above $10^{-4}$, the evolution of nitric oxide occurs, probably due to the decomposition of the nitrous acid which is formed in such solutions. A favorable $H^+$ concentration for the reaction is that given by an acetic acid–acetate buffer.

The effect of temperature on the reaction between the nitrite and the sulfite has been investigated by Raschig.[2] His results may be summarized as follows: at temperatures below 0° only the hydroxylamine disulfonate ion is formed, at temperatures above 5° further reduction to the amine trisulfonate ion occurs and the latter reaction becomes rapid at room temperature. From these facts it is evident that the temperature must be kept low during the preparation of the disulfonate and excess sulfite should be removed before hydrolysis.

Excess nitrite should be avoided as Raschig[3] has shown that nitrous

[1] Divers and Haga, *J. Chem. Soc.*, **69**, 1665 (1896); Adams and Kamm, THIS JOURNAL, **40**, 1283 (1918).

[2] Raschig, "Schwefel- und Stickstoffstudien," Verlag Chemie, Berlin, 1924, p. 8.

[3] Raschig, *ibid.*, p. 7.

oxide is evolved if the disulfonate is hydrolyzed in the presence of nitrites due to a reaction between the monosulfonate and the nitrite. The difficulties due to excess sulfite or nitrite may be avoided by using the potassium salts. The potassium salt of hydroxylamine disulfonic acid is sparingly soluble and precipitates out so that it may be separated from any excess of either reagent.[4] The salt may then be hydrolyzed without danger of side reactions.

The following procedure is recommended for the preparation of hydroxylamine hydrochloride. Weigh out one mole of commercial potassium nitrite and 1.1 to 1.2 moles of potassium acetate. Dissolve these salts in about 200 cc. of ice water and add about 1500 g. of finely chipped ice. Agitate the mixture thoroughly and pass in sulfur dioxide gas until the odor indicates that an excess has been added. During the reaction practically all of the ice will be melted; care should be taken, however, to have some ice present at all times so as to insure keeping the temperature below 0°. Filter out the precipitated potassium hydroxylamine disulfonate with a Büchner funnel and wash the precipitate with ice water. Four washings of about 50 cc. each are usually sufficient to remove all sulfites and acetates from the precipitate. The yields of disulfonate obtained in this way vary with the volume of solution used but are usually approximately 85%. The losses can be accounted for as principally due to the solubility of the salt. The disulfonate is hydrolyzed by placing it in about 1 liter of approximately 0.5 *N* hydrochloric acid and heating to 100° for about two hours. Tests show that under these conditions the hydrolysis is complete in that time; if no acid is added, a longer time should be allowed. The sulfate formed is removed by adding 0.9 mole of barium chloride while the solution is still hot and filtering out the precipitated barium sulfate. The filtrate is evaporated to dryness and the hydroxylamine hydrochloride extracted from the residue by absolute alcohol. The loss of hydroxylamine on hydrolysis by this method is negligible, so the net yield of the hydroxylamine hydrochloride is approximately 85% of the theoretical.

From the results we have obtained with this preparation we may conclude that nitrites react practically quantitatively with bisulfite under the conditions which have been stated to give the hydroxylamine disulfonate ion. Furthermore, the hydrolysis of the disulfonic acid to hydroxylamine is quantitative if carried out in the absence of sulfites or nitrites.

## Summary

A method of preparing hydroxylamine from nitrites by the reduction with sulfite so as to give an 85% yield has been described. The high

[4] An approximate value for the solubility of potassium hydroxylamine disulfonate, $HON(SO_3K)_2 \cdot 2H_2O$, obtained in this Laboratory is 23.0 ± 0.5 g. or 0.075 mole per liter at 0°.

yield is due to the elimination of side reactions by precipitating the potassium salt of hydroxylamine disulfonic acid and separating it from the excess sulfite before hydrolysis.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 275]

# THE COMPARATIVE IONIZATION OF SELENIC AND SULFURIC ACIDS

BY M. S. SHERRILL AND E. H. LYONS, JR.

RECEIVED NOVEMBER 6, 1931 PUBLISHED MARCH 5, 1932

## Introduction

There is much evidence to indicate that sulfuric acid in moderately dilute aqueous solution is substantially completely ionized with respect to its first hydrogen, but only partly with respect to its second. Thus, Sherrill and Noyes,[1] by combining conductance and transference data of sulfuric acid at different concentrations, have estimated the ionization of $HSO_4^-$ ion in sulfuric acid solutions at 25° to vary from 96% at an acid concentration 0.0005 normal to 34.5% at 0.1 normal. The corresponding value of the ionization constant of the $HSO_4^-$ ion was computed to be 0.0115. In making these calculations, it was assumed that the mobility and the activity coefficient of any given ion is, at a definite temperature, determined solely by the ionic strength of the solution.

It is generally assumed that selenic acid closely resembles sulfuric acid in its ionization relations. The physico-chemical evidence of this is very limited, but certain approximate conclusions may be drawn from a comparison of the equivalent conductances of the two acids and their acid salts shown in the following table.[2]

TABLE I

EQUIVALENT CONDUCTANCES AT 25°

| Substance | 0.002 | 0.005 | 0.01 | 0.02 | 0.05 | 0.1 | 0.20 | 0.5 |
|---|---|---|---|---|---|---|---|---|
| $Na_2SO_4$ | 122.1 | 117.3 | 112.4 | | | | | |
| $Na_2SeO_4$ | 117.3 | 113.7 | 109.4 | | | | | |
| $H_2SO_4$ | 390.3 | 364.9 | 336.4 | 308.0 | 272.6 | 250.8 | 234.3 | 222.5 |
| $H_2SeO_4$ | 384 | 366 | 349 | 328 | 295 | 272 | 253 | 233 |

These values indicate that the mobilities of the sulfate ion and selenate ion are approximately the same, and that in dilute solution the hydrogen-ion concentrations in sulfuric acid and selenic acid solution of the same normality are nearly identical, whereas at higher concentrations, such as 0.2 *N*, the hydrogen-ion concentration is slightly greater in the selenic

[1] Sherrill and Noyes, THIS JOURNAL, **48**, 1870 (1926).

[2] "International Critical Tables," Vol. VI, pp. 242, 236, 247.

acid solutions, assuming the mobilities of $HSO_4^-$ and $HSeO_4^-$ to be the same.

In order to confirm these conclusions and to compare the activities of hydrogen ion in solutions of selenic acid and sulfuric acid of the same concentration, Small[3] measured the electromotive force at 25° of cells of the type, $H_2$, $H_2SO_4$ or $H_2SeO_4$ ($c$ formal), satd. KCl, $Hg_2Cl_2$ + Hg. The apparatus consisted of a Leeds and Northrup student type potentiometer, with a desk galvanometer, and the Clark[4] form of cell with a specially designed shaker to rock the hydrogen half-cell.

The results of this investigation are summarized in Table II.

TABLE II

ELECTROMOTIVE FORCE AT 25°

| Form. wt. acid in 1000 g. of $H_2O$ | $H_2SO_4$-Cell $E_1$ | $H_2SeO_4$-Cell $E_2$ | Difference $E_1 - E_2$ |
|---|---|---|---|
| 0.1000 | 0.3014 | 0.3001 | 0.0013 volt |
| .2000 | .2859 | .2850 | .0009 |
| .5000 | .2644 | .2628 | .0016 |
| 1.000 | .2469 | | |

The values for the electromotive force correspond to a barometric pressure of 754 mm. At concentrations of selenic acid above 0.5 formal no reliable results could be obtained owing to reduction of selenic acid by hydrogen at the platinized electrode. The differences in electromotive force, recorded in the last column, can be regarded as a measure of the difference in the electrode potentials only under the assumption that the two liquid potentials counterbalance each other. As this assumption is approximately correct, the small differences of only about one millivolt indicate that the activities of hydrogen ion in solutions of selenic and sulfuric acid of the same concentration are substantially equal.

In the present investigation, which was a continuation of Small's work, the electromotive force of cells of the following type was measured

Pt, Quinhydrone (Satd.) + $H_2SO_4$($c$ formal), $H_2SeO_4$($c$ formal) + Quinhydrone (Satd.), Pt.

In some cases the solution at the electrode was saturated not only with quinhydrone, but also with quinone, thus converting the quinhydrone electrode into the quino-quinhydrone electrode of Biilmann.[5]

In such a cell, with the two acids at the same concentration, the liquid potential is practically equal to zero, so that the electromotive force of the whole cell may be considered equal to the difference between the two electrode potentials. Since each of these, as shown below, is practically determined by the activity of the hydrogen ion in the solution,

[3] Small, Thesis M. I. T., 1927, unpublished.

[4] Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 2d ed., 1923, pp. 180–185.

[5] Biilmann, *Bull. soc. chim.*, **41**, 151 (1927).

the observed electromotive force furnishes a measure of the relative hydrogen-ion activities in sulfuric acid and in selenic acid solutions of the same concentration.

The exact expression for the electrode potential is given by the well-known equation

$$E = E_0 + \frac{RT}{F} \ln [H^+] - \frac{RT}{2F} \ln \frac{[C_6H_4O_2]}{[C_6H_4(OH)_2]}$$

in which $E_0$ is a constant, the molal electrode potential of the reaction of oxidation, $C_6H_4(OH)_2 = C_6H_4O_2 + 2H^+ + 2E^-$, and the symbols $[H^+]$, $[C_6H_4(OH)_2]$, and $[C_6H_4O_2]$ represent the activities of the hydrogen ion, of hydroquinone and of quinone, respectively, in the solution at the inert metal electrode. With the quinhydrone electrode, the last term is practically zero, since hydroquinone and quinone are produced in the solution in equimolal quantities and have therefore almost equal activities. With the quino-quinhydrone electrode this term has a constant value, since the activity of the hydroquinone and also that of the quinone becomes definitely fixed by the presence of the two solids in contact with the solution.

In this investigation the acid concentration was varied from 0.01 to 0.8 formal. As will be shown later, the hope of obtaining with such electrodes reliable results at concentrations above 0.5 formal was not realized. The extension of the work to concentrations below 0.1 formal is of importance, since, as already pointed out, the ionization of the second hydrogen of sulfuric acid changes rapidly with the concentration in these more dilute solutions.

**Preparation of Materials and Solutions.**—The selenic acid was prepared from a sample of commercial selenium. Following the method of Dennis and Koller[6] the crude selenium was dissolved in an excess of concentrated nitric acid, the solution was evaporated to dryness, the residue moistened with water and the liquid again evaporated to remove the excess of nitric acid. The selenous acid thus obtained was recrystallized six times from water. Selenic acid was prepared from this pure selenous acid by the method of Meyer and Moldenhauer.[7] This consists in oxidizing the selenous acid to selenic acid by means of chloric acid, prepared by the interaction of barium chlorate and sulfuric acid, and then concentrating the resulting solution *in vacuo*. The final product showed no test for selenous or sulfuric acid.

A stock solution of selenic acid was made from this concentrated acid, and standardized against sodium carbonate, using methyl orange as indicator. The solutions used in the cells were prepared from the stock solution by suitable dilution with water. All concentrations are expressed as formula weights of selenic acid, $H_2SeO_4$, per 1000 g. of water.

[6] Dennis and Koller, THIS JOURNAL, **41**, 952 (1913).

[7] Meyer and Moldenhauer, *Z. anorg. allgem. Chem.*, **116**, 192–200 (1921).

The solutions of sulfuric acid of known concentration were prepared from concentrated C. P. sulfuric acid by the procedure just described for selenic acid.

The quinhydrone was obtained from the Eastman Kodak Co. It melted at 168–170°.

**Apparatus and Method of Measurement.**—The potentiometer was a Leeds and Northrup student type with a desk galvanometer. It was standardized through the use of a carefully calibrated Weston standard cell.

The electrode vessels were of the usual calomel cell type, 25 mm. in diameter, 90 mm. long, with side arms of 8-mm. tubing constricted at the tip to 5 mm. Each half-cell was fitted with a rubber stopper bearing three electrodes, two of platinum foil, 10 mm. by 20 mm., and one of gold foil, 8 mm. by 25 mm. Each platinum electrode was welded to a short platinum wire and sealed to a glass tube. The connection to the potentiometer was made by means of mercury and copper wire. The gold electrode was welded to a longer gold wire, which was sealed into an open glass tube by means of sealing wax, and connected to the potentiometer by copper wire.

Various methods of cleaning the electrodes were tried before reproducible values of the electromotive force could be obtained. Biilmann's method[8] of heating the electrodes to redness in an alcohol flame was the one finally adopted. When by this procedure the potential difference between each pair of electrodes immersed in the same acid solution was reduced to a value less than a tenth of a millivolt, the electrodes were considered to be satisfactory for use.

In preparing the quinhydrone half-cells a small quantity of quinhydrone (10–50 mg.) was stirred with the solution to form a paste, which was then shaken with more of the solution in the electrode vessel. With the metal electrodes inserted, the vessel was approximately half filled with solution. For the quino-quinhydrone half-cells a similar procedure was followed, using an excess of one part of quinhydrone to five parts of quinone. With these cells only the platinum electrodes were used. They were bent upward in the shape of a hook so as to catch and hold some of the two solid phases at the metal surface, thus insuring saturation.

The liquid junction in the cell was made as follows. The half-cells with the side arms projecting into an empty 50-cc. beaker were immersed, as far as such an arrangement would permit, in a water thermostat at 25°, within 0.05°. A drop was formed at the tip of each side arm and then removed by touching it with a clean stirring rod. The bridge solution of selenic acid, which was slightly more dense than the sulfuric acid solution of equal concentration, was flowed into the beaker until it rose

[8] Biilmann, *Ann. chim.*, [9] **15,** 109 (1921).

above the tips of the side arms. To minimize convection currents in establishing the liquid junction, the one side arm was protected by a small glass tube which acted as a collar.

In measuring the electromotive force readings were taken for each possible combination of electrode pairs. Thus, with three electrodes in each quinhydrone half-cell, nine different combinations were possible, and correspondingly nine separate readings were taken. The electromotive force recorded in the tabulation of results represents in each case the average of a number of such measurements with freshly made solutions in the cells.

**Results of the Electromotive Force Measurements.**—The results of the measurements with cells of the type Pt, Quinhydrone-$H_2SO_4$ ($c$ formal), $H_2SeO_4$ ($c$ formal)—Quinhydrone, Pt are shown in Table III.

TABLE III

ELECTROMOTIVE FORCE OF CELLS CONTAINING BOTH SULFURIC AND SELENIC ACIDS AT 25° IN MILLIVOLTS

| Formal concn. acid ($c$) | Quinhydrone electrodes | Quino-quinhydrone electrodes | Formal concn. acid ($c$) | Quinhydrone electrodes | Quino-quinhydrone electrodes |
|---|---|---|---|---|---|
| 0.0100 | 0.08 | .. | 0.4000 | 0.40 | 0.01 |
| .0250 | .15 | .. | .5000 | .00 | .11 |
| .0500 | .39 | .. | .6000 | ... | (1.0) |
| .1000 | .02 | .. | .7000 | ... | (3.3) |
| .2000 | .30 | .. | .8000 | ... | (1.4) |
| .3000 | .06 | 0.23 | | | |

Very reproducible results for the electromotive force were obtained with quinhydrone electrodes up to an acid concentration 0.5 formal. The results recorded represent not only an average of the separate values of electromotive force obtained with the different electrode pair combinations, but also an average of the final values thus obtained with freshly made solutions in the cells. The electromotive force differed from zero seldom by more than one or two tenths of a millivolt; and though these small values were almost all positive it is doubtful whether the deviation from zero is really significant.

At higher concentrations the results were less reproducible, particularly with the gold electrodes. For this reason a series of measurements was made with quino-quinhydrone electrodes. It was still found impossible with acid concentrations above 0.5 formal to obtain results reproducible to less than several millivolts. The values recorded in parentheses, though representing averages, are accordingly to be regarded as unreliable.

These results indicate that for the range of concentration from 0.01 to 0.5 formal the activities of hydrogen ion in solutions of selenic acid and of sulfuric acid of the same concentration are very nearly equal. It is correspondingly probable that for this concentration range the ionization re-

lations of selenic acid are almost identical with those of sulfuric acid. Hence, accepting the estimates of Sherrill and Noyes[1] in the case of sulfuric acid as applicable to selenic acid, the statement may be made that selenic acid at a concentration 0.5 formal exists mainly in the form of the ions, $H^+$ and $HSeO_4^-$, whereas, at a concentration 0.01 formal, the ion $HSeO_4^-$ is about 67% dissociated into $H^+$ and $SeO_4^=$ ions. As the ionization constant of $HSO_4^-$ was found to be 0.0115, that of $HSeO_4^-$ is of nearly the same magnitude.

## Summary

The electromotive force of cells of the type, Pt, Quinhydrone $H_2SO_4$ ($c$ formal), $H_2SeO_4$ ($c$ formal) Quinhydrone, Pt, was measured at 25° and found to be substantially equal to zero over a range of acid concentration in the cell from 0.01 to 0.5 formal. At higher acid concentrations, 0.6 to 0.8 formal, reproducible results could not be obtained. The conclusion was drawn that in dilute solution the ionization relations of selenic acid are almost identical with those of sulfuric acid.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

# AN EXTENSION OF THE ISOAMYL ALCOHOL SEPARATION OF THE ALKALI AND ALKALINE EARTH METALS TO THE LESS COMMON ALKALIES, LITHIUM, RUBIDIUM AND CESIUM

BY HERMAN YAGODA[1]

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Gooch has shown that isoamyl alcohol can be applied to the quantitative separation of lithium from sodium and potassium by its solvent action upon the chlorides,[2] and Browning has used the same alcohol for bringing about a separation of calcium from barium and strontium using the nitrates[3] and of strontium from barium using the bromides.[4] Detailed schemes for the qualitative analysis of the entire alkali group have been developed by Ato and Wada,[5] and Noyes and Bray.[6] These methods were designed to detect small quantities of any one of the alkalies when present in admixture with large amounts of the others. Because of the similar solubilities of the salts of potassium, rubidium and cesium, the

[1] Formerly a fellow at the University.

[2] F. A. Gooch, *Am. Chem. J.*, **9**, 33 (1887).

[3] P. E. Browning, *Am. J. Sci.*, **43**, 50 and 314 (1892).

[4] P. E. Browning, *ibid.*, **44**, 459 (1892).

[5] Sunao Ato and Isaburo Wada, *Sci. Papers Inst. Phys. Chem. Research*, **4**, 261 (1926), in English; *Z. anal. Chem.*, **72**, 50 (1927).

[6] Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," 1927, p. 246.

procedures are lengthy, involve the use of uncommon reagents, and demand considerable skill and experience from the analyst. In view of their researches, it is doubtful whether a simple scheme of ion analysis can be devised for the general mixture of alkalies.

In a previous paper[7] I have extended the application of isoamyl alcohol to the qualitative analysis of the common alkali and alkaline earth metals by a primary division of the bromide salts into two groups. It was thought advisable to study the distribution of lithium, rubidium and cesium bromides when the mixture, together with the salts of the common alkali and alkaline earths, was treated with the solvent in order to determine how their presence would conflict with the detection of the common elements; and if it were possible to effect a simple separation of the rare alkalies therewith.

Measurements of the solubility of the rare alkali bromides revealed that the lithium salt was very soluble, but that only 0.05 and 0.06 mg. of the respective rubidium and cesium bromides dissolved in 1 cc. of isoamyl alcohol at 25°. Lithium was found to accompany the members of the soluble group, magnesium, calcium and strontium, whereas rubidium and cesium, when present in appreciable amounts, separated with the sodium, barium and potassium bromides. The separation into two groups, as described in the first paper, involved the extraction of the anhydrous bromides with isoamyl alcohol. It was found more satisfactory to dissolve the salts in a minimum of water, and to cause the precipitation of the insoluble group by boiling the solution with an excess of isoamyl alcohol until the water was expelled (1). Experiments showed that this caused the precipitation of 1 mg. of all the insoluble bromides and kept in solution 300 mg. of lithium, calcium and magnesium bromides, but only 100 mg. of the strontium salt.

The presence of lithium in the soluble group does not materially alter the procedure for the separation and detection of calcium and magnesium. In the separation of strontium from calcium by the action of 16 *N* nitric acid, it was found that when large quantities of lithium were present, small quantities of the nitrate remained behind with the strontium. This makes a further confirmatory test for strontium desirable (2). Lithium is detected in the filtrate, after the usual separation of calcium as the oxalate, by precipitation of lithium stearate from an isoamyl alcohol solution (3). By using the nitrate salts, instead of the chlorides as recommended by Caley,[8] traces of strontium do not confuse the test for lithium because strontium nitrate is not extracted by the isoamyl alcohol.

The first step in the analysis of the insoluble group of bromides is to boil the mixture with 1–2 cc. of 95% ethyl alcohol containing 1–2 drops

[7] H. Yagoda, THIS JOURNAL, **52,** 3068 (1930).

[8] E. R. Caley, *ibid.*, **52,** 2754 (1930).

of 8 *N* hydrobromic acid. The solubilities of rubidium and cesium bromides in this medium at 25° are 1.8 and 2.1 mg. per cc., respectively. When the volume of the solvent is 2 cc. quantities of the rare alkalies in excess of 1 mg. each will accompany the potassium in the insoluble sub-group. On addition of 12 *N* hydrochloric acid to the soluble sub-group, sodium and barium chlorides precipitate, the traces of potassium, rubidium and cesium chlorides remaining dissolved. The sodium and barium chlorides are filtered off and washed with 12 *N* hydrochloric acid (4). The filtrate is combined with the solution obtained by dissolving the insoluble sub-group in 5 cc. of hot water. The combined liquid is freed from alcohol and acid by evaporation to dryness, the residue is redissolved in 5 cc. of water, the solution precipitated with sodium cobaltinitrite reagent and filtered. This yellow precipitate consists, in general, of potassium, rubidium and cesium cobaltinitrites. The presence or absence of the rare alkalies is best ascertained by spectroscopic analysis of the flame spectrum. If a knowledge of their relative quantities is desired, the cobaltinitrite mixture can be separated by following procedure 166 as described by Noyes and Bray.[9]

## Notes on the Procedure

(1) The mixed bromides taken for analysis should not exceed 100 mg. in weight. Add hot water dropwise until it just dissolves, then add 10 cc. of isoamyl alcohol, boil down to a volume of 2 cc., add 1 drop of 8 *N* hydrobromic acid and 1 cc. of the cold solvent, cool, filter and wash the precipitate with about 1 cc. of isoamyl alcohol. In order that the liquid may boil quietly when water is present in the solvent, a stirring rod terminating in a capillary tip is placed in the beaker. The rod is made by drawing out a 4-mm. glass tube to a coarse capillary of total length 10 cm. and sealing a solid constriction in the glass about 1 cm. from the capillary end.

(2) The salt insoluble in the nitric acid is filtered off, dried by air suction, redissolved in 0.5 cc. of water, and the solution is boiled with 5 cc. of isoamyl alcohol until the volume is reduced to 2 cc. If strontium is present, strontium nitrate will precipitate out.[10] Both lithium and calcium nitrates are soluble in isoamyl alcohol.

(3) Evaporate the filtrate from the calcium oxalate to dryness, add 1 cc. of 16 *N* nitric acid, heat until excess ammonium oxalate is decomposed, cool, add 2–3 cc. of isoamyl alcohol, boil, cool and filter into a 10-cc. test-tube. To the filtrate add 2.5 times its volume of a freshly prepared 2% solution of ammonium stearate in isoamyl alcohol. A white precipitate forming is lithium stearate.

(4) The chlorides of sodium and barium are examined in the flame. If the color reveals the presence of both, dissolve the salts in 2 cc. of water, add a few drops of 6 *N* sulfuric acid, boil, cool and filter off any barium sulfate formed. Sodium is detected in the filtrate by the addition of 1 cc. of ethyl alcohol and 3 cc. of zinc uranyl acetate reagent, a greenish-yellow crystalline precipitate forms. This reagent, developed by Kolthoff,[11] consists of 10 g. of $UO_2Ac_2 \cdot 2H_2O$, 30 g. of $ZnAc_2 \cdot 3H_2O$, 9 g. of 30% acetic

[9] Ref. 6, p. 260.

[10] P. E. Browning, *Am. J. Sci.*, **43**, 387 (1892).

[11] H. H. Barber and I. M. Kolthoff, THIS JOURNAL, **50**, 1625 (1928); I. M. Kolthoff, *Z. anal. Chem.*, **70**, 397 (1926).

acid and 130 g. of water; the two salts are dissolved separately in equal volumes of water, the acid is added and the mixture filtered.

### Identification of the Alkali and Alkaline Earth Metals

Concentrate filtrate from the 3d analytical group down to 5 cc. Transfer to a 30-cc. beaker, add 3 cc. of 16 *N* $HNO_3$ and evaporate to dryness. Add 2 cc. of 8 *N* HBr, boil off acid and cool dry residue. If this is large, dissolve only a 100-mg. portion in a minimum of hot water, add 10 cc. of isoamyl alcohol, boil down to a volume of 2 cc., add 1 drop of 8 *N* HBr and 1 cc. of isoamyl alcohol, cool, filter and wash precipitate with small volume of solvent.

### Analysis of Precipitate

*Precipitate:* NaBr, $BaBr_2$, KBr, RbBr and CsBr. Make flame test. Boil dry residue with 2 cc. of 95% ethyl alcohol, add 2 drops of 8 *N* HBr, cool and filter.

| | | |
|---|---|---|
| *Precipitate:* Chiefly K, Rb and Cs bromides. Wash with 1 cc. of 95% ethyl alcohol. Dissolve in 5 cc. of hot water. | *Filtrate:* Contains NaBr, $BaBr_2$ and traces of KBr, RbBr and CsBr. Add 0.5 cc. of 12 *N* HCl dropwise, cool and filter. | |
| | *Precipitate:* NaCl and $BaCl_2$. Dissolve in 2 cc. of water, add a few drops of 6 *N* $H_2SO_4$, boil and filter. A white precipitate is $BaSO_4$. To the filtrate add 1 cc. of 95% ethyl alcohol and 3 cc. of zinc uranyl acetate reagent. A greenish-yellow precipitate confirms presence of sodium. | *Filtrate:* RbCl, CsCl and KCl. Evaporate to dryness. Combine with main portion of bromide salts. Add a 25% solution of $Na_3Co(NO_2)_6$ dropwise, filter, wash with 50% ethyl alcohol. Examine spectroscopically. |

### Analysis of Filtrate

*Filtrate:* $MgBr_2$, $SrBr_2$, $CaBr_2$ and LiBr. Boil off the isoamyl alcohol, add 1 cc. of 16 *N* $HNO_3$ and evaporate to dryness. *Residue:* $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$ and $LiNO_3$. Heat strongly, cool, add 3 cc. of water, boil and filter.

| | | |
|---|---|---|
| *Residue:* MgO and $Mg(OH)_2$. Redissolve in 1 cc. of 6 *N* HCl, add 1 cc. of 1 *N* $(NH_4)_2HPO_4$ and 2 cc. of 16 *N* $NH_4OH$. A white crystalline precipitate of $MgNH_4PO_4$ confirms presence of magnesium. | *Filtrate:* $Sr(NO_3)_2$, $Ca(NO_3)_2$ and $LiNO_3$. Evaporate to dryness, cool, add 1 cc. of 16 *N* $HNO_3$, raise to a boil, add another 1-cc. portion of acid, cool and filter, moistening paper with nitric acid and using suction. | |
| | *Precipitate:* $Sr(NO_3)_2$. Dry, dissolve in 0.5 cc. of hot water, add 5 cc. of isoamyl alcohol, boil until volume is 2 cc. The appearance of a white precipitate confirms presence of strontium. | *Filtrate:* $Ca(NO_3)_2$ and $LiNO_3$. Boil off excess acid, redissolve in 3 cc. of water, make ammoniacal, add 1 cc. of saturated $(NH_4)_2C_2O_4$ solution. A white precipitate confirms calcium. |
| | | Filter, evaporate filtrate to dryness, heat until excess oxalate is volatilized, cool, add 2 cc. of isoamyl alcohol, boil, cool and filter. To filtrate add 5 cc. of a freshly prepared 2% ammonium stearate solution in isoamyl alcohol. A white precipitate is lithium stearate. |

## Summary

In the qualitative analysis for all the alkali and alkaline earth metals, isoamyl alcohol acting on a mixture of the bromides effects a primary separation of the elements into two groups. The soluble group consists of magnesium, strontium, calcium and lithium bromides; it is further separated by simple methods involving the specific behavior of the nitrates upon ignition, solution in nitric acid and precipitation from isoamyl alcohol solution. The insoluble group, consisting of sodium, barium,

potassium, rubidium and cesium bromides, is treated as described in a previous paper, the rare alkalies being provided for by segregating them into one group along with potassium. The procedure, based on quantitative separations of the individual elements, has been tested and found satisfactory for a rapid identification of the alkali and alkaline earth metals when present in mixture.

NEW YORK CITY, N. Y.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 292]

# THE NATURE OF THE CHEMICAL BOND. III. THE TRANSITION FROM ONE EXTREME BOND TYPE TO ANOTHER[1]

BY LINUS PAULING

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A question which has been keenly argued for a number of years is the following: if it were possible continuously to vary one or more of the parameters determining the nature of a system such as a molecule or a crystal, say the effective nuclear charges, then would the transition from one extreme bond type to another take place continuously, or would it show discontinuities? For example, are there possible all intermediate bond types between the pure ionic bond and the pure electron-pair bond? With the development of our knowledge of the nature of the chemical bond it has become evident that this question and others like it cannot be answered categorically. It is necessary to define the terms used and to indicate the point of view adopted; and then it may turn out, as with this question, that no statement of universal application can be made.

In the following sections, after a discussion of the properties of ionic compounds and compounds containing electron-pair bonds, the transition from one extreme to the other is considered. It is concluded that in some cases the transition could take place continuously, whereas in others an effective discontinuity would appear.

## Bond Type and Atomic Arrangement

The properties of a compound depend on two main factors, the nature of the bonds between the atoms, and the nature of the atomic arrangement. It is convenient to consider that actual bonds approach more or less closely one or another of certain postulated extreme bond types (ionic, electron-pair, ion-dipole, one-electron, three-electron, metallic, etc.), or

[1] A part of the material of this paper was presented to the American Chemical Society at Buffalo, New York, September 2, 1931, under the title "The Structure of Crystals and the Nature of the Chemical Bond."

are intermediate between one extreme type and another, or involve two or more co-existent types. The satisfactory description of the atomic arrangement in a crystal or molecule necessitates the complete determination of the position of the atoms relative to one another. Sometimes individual details of the atomic arrangement are of interest; for example, in case the atoms are held together in part by strong bonds and in part by very weak bonds, it is instructive to mention the type of atomic aggregate formed by the strong bonds (finite molecules or complex ions, or molecules or complex ions of very great extent in one, two or three dimensions). In other cases the number of nearest neighbors of each atom (its coördination number) and their relative positions are items of interest.

There is, of course, a close relation between atomic arrangement and bond type. Thus the four single bonds of a carbon atom are directed toward the corners of a tetrahedron. But tetrahedral and octahedral configurations are also assumed in ionic compounds, so that it is by no means always possible to deduce the bond type from a knowledge of the atomic arrangement.

An abrupt change in properties in a series of compounds, as in the melting points or boiling points of halides, is often taken as indicating an abrupt change in bond type. Thus of the fluorides

| | $NaF$ | $MgF_2$ | $AlF_3$ | $SiF_4$ | $PF_5$ | $SF_6$ |
|---|---|---|---|---|---|---|
| M. p. | 980° | 1400° | 1040° | −77° | −83° | −55° |

those of high melting points have been described as salts, and the others as covalent compounds. Actually the Al–F bond is no doubt closely similar to the Si–F bond. The abrupt change in properties between $AlF_3$ and $SiF_4$ is due to a change in atomic arrangement. In NaF, $MgF_2$ and $AlF_3$ the coördination number of the metal (six) is greater than the stoichiometric ratio of non-metal to metal atoms, so that each non-metal atom or ion is held jointly by two or more metal atoms or ions, resulting in high melting and boiling points. In $SiF_4$, $PF_5$ and $SF_6$ the coördination number is just equal to this ratio. The discrete molecules of composition given by the formulas are held only loosely together, and the substances melt and boil easily. As pointed out long ago by Kossel, this ease of fusion and volatilization would be expected for symmetrical ionic molecules, and is not sound evidence for the presence of electron-pair bonds. Volatility does not depend mainly on bond type, but on the atomic arrangement and the distribution of bonds.

## The Ionic Bond

The theoretical treatment of the properties of ionic crystals and molecules has been carried farther than that of other types of atomic aggregates. The Born theory of crystal energy permits the calculation to within

a few per cent. of the energy of dissociation of an ionic crystal into gaseous ions when the structure of the crystal and the equilibrium interionic distances are known. Moreover, it is now possible to predict interionic distances to within 2 or 3%, with the use either of Goldschmidt's set[2] of ionic radii, derived from the experimentally observed interionic distances in crystals of simple structure, many of which were prepared for the first time and studied with x-rays in his Mineralogical Institute in Oslo, or of a closely similar set obtained[3] by a method of treatment based on the theory of the electron distribution in atoms and ions. The screening constants[4] used in the derivation of this set were derived in part theoretically (for light ions) and in part from the experimental values of the mole refraction of atoms and ions. It has been recently found[5] that screening constants can be obtained purely from observed ionization potentials

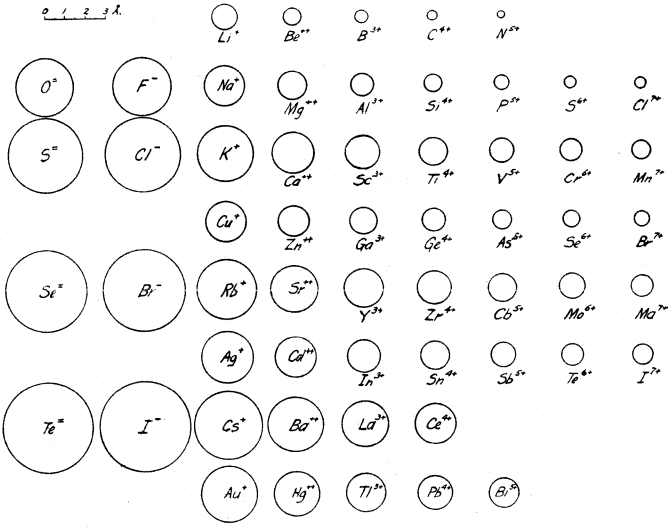



Fig. 1.—The sizes of spherically-symmetrical ions. The radii of the spheres are taken equal to the crystal radii of the ions.

and x-ray term values. The new set of screening constants is in nearly complete agreement with the old one, which gives a feeling of confidence in this method of treating the properties of many-electron atoms and monatomic ions.

The fundamental character of the understanding of ionic crystals which has been obtained is seen from the nature of the dependence of ionic radii on atomic number, shown in Fig. 3 of Ref. 3. The univalent radii lie on

[2] V. M. Goldschmidt, "Verteilungsgesetze der Elemente," Oslo, 1926, Vol. VII.

[3] Linus Pauling, THIS JOURNAL, **49**, 765 (1927).

[4] Linus Pauling, *Proc. Roy. Soc.* (London), **A114**, 181 (1927).

[5] Linus Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

a smooth curve for each isoelectronic sequence; these are corrected in a systematic way for the effect of increasing Coulomb attraction in pulling highly charged ions more closely together to obtain the crystal radii. As is seen in Fig. 1, anions are very large, larger than all cations except those of the alkali metals. Moreover, the anions occur in pairs of nearly the same radius, $O^=$ and $F^-$, etc. This is the reason that hydroxyl ion and fluorine ion so often replace each other isomorphously in minerals, such as topaz, $Al_2SiO_4(OH,F)_2$. (The proton has little effect on the crystal radius.)

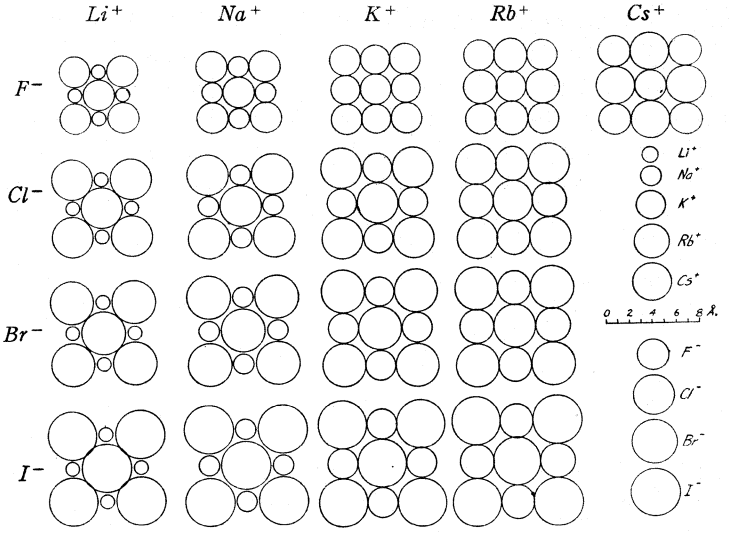



Fig. 2.—The arrangement of ions in cube-face layers of alkali halide crystals with the sodium chloride structure.

The equilibrium interionic distances and accordingly the properties of crystals are influenced not only by the sum of the radii of anion and cation, but also by their ratio, as discussed by Van Arkel and especially by Goldschmidt. This is shown in Fig. 2, representing the alkali halide crystals with the sodium chloride structure. In most of the crystals the anions and cations are in contact. In LiCl, LiBr and LiI, however, the anions are so large relative to the cations that they come into mutual contact, and the size of the unit of structure is determined by the anion radius alone, the cations being left to rattle around in the interstices. This determination of the dimensions of the units and the arrangement of the anions by the anions alone has been especially discussed by W. L. Bragg and co-workers,[6] who have utilized it extensively in studying the structures of silicate minerals. In LiF, NaCl, NaBr and NaI the phe-

[6] W. L. Bragg and J. West, *Proc. Roy. Soc.* (London), **A114**, 450 (1927).

nomenon of *double repulsion* (anion–cation as well as anion–anion repulsion operative) causes the unit to be larger than would be expected from either the anion–cation or anion–anion radius sum. Anion contact and double repulsion have a striking effect on the course of the properties of the alkali halides, particularly the melting points and boiling points.[7]

The conception of simple ionic crystals as coördinated structures, developed by Ewald, Goldschmidt and others, has been shown to be applicable to complex crystals by W. L. Bragg's determination of the structure of a number of the silicate minerals,[8] and through the study of brookite[9] and topaz[10] led ultimately to the formulation of a set of principles governing the structure of complex ionic crystals.[11] These rules may be illustrated by the application of one of them to the question of the isomorphous replacement of $OH^-$ by $F^-$. The electrostatic valence rule states that in a stable crystal each anion tends to have its charge balanced by the electrostatic bonds of adjacent cations, the strength of a bond from a cation being taken as the ratio of its charge to its coördination number; in other words, the valence of the cation is considered as evenly distributed among the anions coördinated about it. Thus $Si^{4+}$ with coördination number 4 has bonds of strength 1, $Al^{3+}$ with coördination number 6, bonds of strength $1/2$. In topaz, $Al_2SiO_4(OH,F)_2$; chondrodite, $Mg_5Si_2O_8(OH,F)_2$; etc., the $OH^-$ ions are in positions of total strength of bonds from cations other than hydrogen equal to 1, and so they may be replaced by $F^-$ ions. But in staurolite, $H_2FeAl_4Si_2O_{12}$, there are not two oxygens in positions of total bond strength 1, but rather four with total bond strength 3/2, suggesting strongly the presence of two $[OHO]^{\equiv}$ groups. In consequence fluorine should not be expected to occur in this mineral, in agreement with observation.

## The Electron-Pair Bond

It was shown by G. N. Lewis and Irving Langmuir that unique electronic structures involving electron-pair bonds can be assigned with considerable certainty to a great many molecules and crystals. For many others, however, decision between two or more alternative structures has been difficult; moreover, the theory has not led to predictions regarding atomic arrangements other than the postulated tetrahedral arrangement of four electron pairs. Considerable further progress has now been made possible through the deduction from the quantum mechanics of a set of rules regarding electron-pair bonds, and in particular the discovery of a simple semi-quantitative treatment of bond eigenfunctions which

[7] Linus Pauling, THIS JOURNAL, **50**, 1036 (1928).

[8] W. L. Bragg, *Z. Krist.*, **74**, 237 (1930).

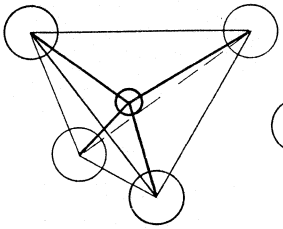
[9] Linus Pauling and J. H. Sturdivant, *ibid.*, **68**, 239 (1928).

[10] Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 603 (1928).

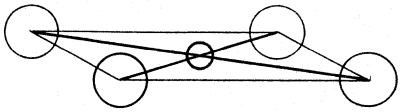
[11] Linus Pauling, THIS JOURNAL, **51**, 1010 (1929).

gives much information regarding the strength and mutual orientation of the bonds which can be formed by various atoms.[12]

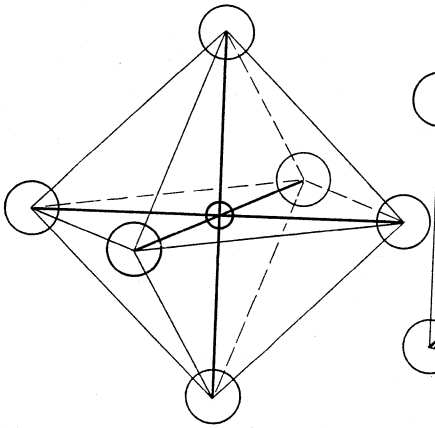
It has been found that the strength and direction of an electron-pair bond formed by an atom are determined essentially by one electronic eigenfunction. The bond tends to be formed in the direction in which



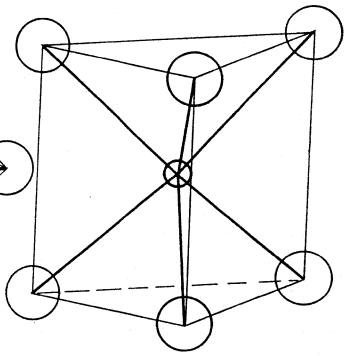
Tetrahedral, $sp^3$ (2.000). C in diamond and compounds. Zn in $[Zn(CN)_4]^=$, etc.



Square, $dsp^2$ (2.694). Ni in $[Ni(CN)_4]^=$, Pd in $[PdCl_4]^=$, Pt in $[PtCl_4]^=$, Au in $[AuCl_4]^-$, etc.



Octahedral, $d^2sp^3$ (2.923). Co in $[Co(CN)_6]^{\equiv}$, Pd in $[PdCl_6]^=$, Pt in $[PtCl_6]^=$, etc.



Trigonal-prismatic, (2.983). Mo in $MoS_2$, and perhaps in $[Mo(CN)_6]^=$.

Fig. 3.—The relative orientations of various electron-pair bonds.

the eigenfunction has its maximum value, and the greater the concentration of the eigenfunction in the bond direction the stronger the bond will be. The spherically-symmetrical $s$ eigenfunction can form a bond in any direction of strength 1 according to the semi-quantitative treatment, and a $p$ eigenfunction a bond of strength 1.732 in either of two opposite directions. But in most atoms which form four or more bonds

[12] (a) Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928); (b) THIS JOURNAL, **53**, 1367 (1931); (c) *Phys. Rev.*, **37**, 1185 (1931); (d) J. C. Slater, *ibid.*, **37**, 481 (1931); **38**, 1109 (1931).

the $s$ and $p$ eigenfunctions do not retain their identity, being instead combined to form new eigenfunctions, better suited to bond formation. The best bond eigenfunction which can be formed from the one $s$ and three $p$ eigenfunctions in a given shell has the strength 2.000. Moreover, three other equivalent bond eigenfunctions can also be formed, and the four bonds are directed toward the corners of a regular tetrahedron (Fig. 3). This result immediately gives the quantum-mechanical justification of the chemist's tetrahedral carbon atom, with all its properties, such as free rotation about a single bond (except when restricted by steric effects) and lack of it about a double bond, and shows that many other atoms direct their bonds toward tetrahedron corners.

The nature of possible bond eigenfunctions involving $d$ eigenfunctions depends on the number of $d$ eigenfunctions available. Bivalent nickel contains eight unshared $3d$ electrons, which require at least four of the five $3d$ eigenfunctions, leaving only one for bond formation. When this is combined with the $4s$ and the three $4p$ eigenfunctions of nearly the same energy, it is found that not five but only four equivalent bond eigenfunctions, of strength 2.694, can be formed, and that these are directed toward the corners of a square. Thus the $[Ni(CN)_4]^=$ ion should have a square rather than a tetrahedral configuration. This was suggested for complexes containing bivalent palladium and platinum by Werner, and was verified by Dickinson[13] by the x-ray study of $K_2PdCl_4$ and $K_2PtCl_4$. We expect a similar configuration for complexes of trivalent copper, silver and gold.

When two $d$ eigenfunctions are available, as in trivalent cobalt, quadrivalent palladium and platinum, etc., six equivalent bond eigenfunctions of strength 2.923 and directed toward the corners of a regular octahedron can be formed. These form the bonds in a great many octahedral complexes.

It is interesting to note, as pointed out to me by Mr. J. L. Hoard, that these considerations lead to an explanation of the stability of trivalent cobalt in electron-pair bond complexes as compared to ionic compounds. The formation of complexes does not change the equilibrium between bivalent and trivalent iron very much, as is seen from the electrode potentials, while a great change is produced in the equilibrium between bivalent and trivalent cobalt.

$$\begin{aligned} Fe^{++} &= Fe^{+++} + E^- && -0.74 \text{ v.} \\ [Fe(CN)_6]^= &= [Fe(CN)_6]^{=} + E^- && -0.49 \text{ v.} \end{aligned} \Big\rangle -0.25 \text{ v.}$$

$$\begin{aligned} Co^{++} &= Co^{+++} + E^- && -1.8 \text{ v.} \\ [Co(CN)_6]^= &= [Co(CN)_6]^{=} + E^- && +0.3 \text{ v.} \end{aligned} \Big\rangle -2.1 \text{ v.}$$

The effect is so pronounced that covalent compounds of bivalent cobalt are difficult to prepare, decomposing water with the liberation of hydro-

[13] R. G. Dickinson, THIS JOURNAL, **44**, 2404 (1922).

gen. The explanation is contained in Fig. 4. In the ions $Co^{++}$, $Co^{+++}$, $Fe^{++}$, and $Fe^{+++}$ there is room for all unshared electrons in the $3d$ subshell or inner subshells. When octahedral bonds are formed only three $3d$ eigenfunctions are left for occupancy by unshared electrons. These are enough for bivalent and trivalent iron and for trivalent cobalt, but they hold only six of the seven electrons of bivalent cobalt. The seventh electron must accordingly occupy an outer unstable orbit, causing the complex to become unstable.

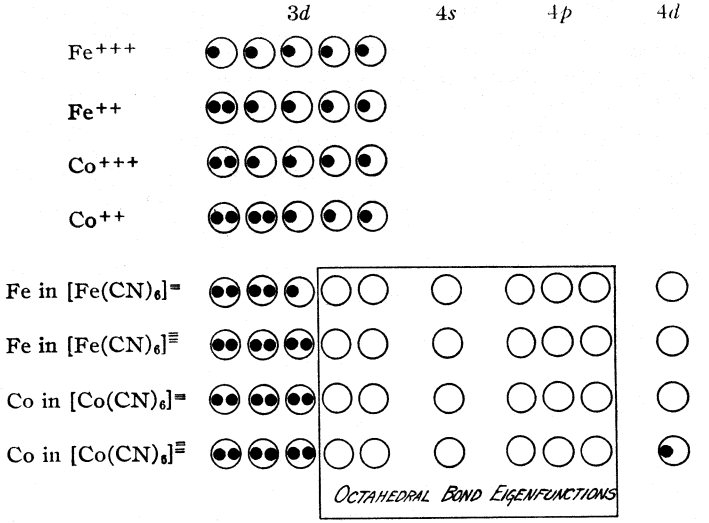



Fig. 4.—A diagram representing the electronic configurations of certain complex ions. Each circle represents a single-electron positional eigenfunction, each dot an electron.

The structure[14] of the mineral molybdenite, $MoS_2$, in which each molybdenum atom is surrounded by six sulfur atoms at the corners of a triangular prism, has long been puzzling, for if the crystal were composed of ions an octahedral arrangement would be more stable, and the large number of octahedral complexes containing electron-pair bonds would suggest an octahedral electron-pair bond structure also. But the molybdenum atom contains only two unshared $d$ electrons, and it has been recently found by Mr. Ralph Hultgren that in this case six equivalent bonds of strength 2.983 (considerably greater than that of octahedral bond eigenfunctions) directed toward the corners of a trigonal prism may be formed. The theoretical ratio of altitude to base of the prism is 1000, while the experimental value is $1.007 \pm 0.038$. It would be interesting to determine whether a similar configuration holds for $[Mo(CN)_6]^=$; a di-substituted complex such as $[Mo(CN)_4Cl_2]^=$ should then exist in three isomeric forms.

[14] R. G. Dickinson and Linus Pauling, THIS JOURNAL, **45**, 1466 (1923).

## The Transition from One Bond Type to Another

The question as to whether or not the transition from one extreme bond type to another would take place continuously as one or more parameters determining the nature of the atoms involved were varied can now, I believe, be satisfactorily answered. The quantum mechanics shows that if, for a polyatomic system having a given atomic arrangement, there are two possible electronic states with nearly the same energy and with the same multiplicity, then it is necessary to consider mixed states, with an eigenfunction for the system formed by linear combination of the eigenfunctions for the first two states. The actual state of the system would lie somewhere between the two postulated extremes. If the states have different multiplicities, however, they cannot be combined with one another (so long as spin-orbit interactions of the electrons are negligible). So although every energy level of a system changes continuously as parameters defining the system are changed, the normal state may show a discontinuity at the crossing of two non-combining levels.

This discussion is most easily made precise by the use of the energy integral. If $\psi$ represents an arbitrary normalized wave function for a system, then the integral

$$E = \int \psi^* H \psi d\tau$$

in which $H$ is the Hamiltonian operator, gives a value of $E$ which must be equal to $W_0$, the energy of the lowest state of the system, or be greater than $W_0$. For $E$ to be equal to $W_0$ it is necessary that $\psi$ be the eigenfunction for the normal state of the system, and the closer $\psi$ approaches this eigenfunction the smaller the difference $E - W_0$ will become. Now let us set up a function $\psi_1$ of the coördinates of the system which represents a conceivable state of the system, for example, a state corresponding to a given Lewis electronic formula for a molecule. We can then evaluate the electronic energy $E_1$ as a function of the internuclear distances by substituting $\psi_1$ for $\psi$ in the above equation. Similarly a function $\psi_2$ corresponding to an alternative electronic formula can be used to calculate $E_2$. If $E_1$ lies far below $E_2$, then the function $\psi_1$ is a much better approximation to the normal state of the system than $\psi_2$, and, in the absence of further alternatives, the electronic formula corresponding to $\psi_1$ is to be accepted. In general, if $\psi_1$ and $\psi_2$ have the same symmetry character and especially the same multiplicity (that is, the same number of unpaired electrons), values of $E$ for a more general function $a\psi_1 + b\psi_2$ should be calculated. When $E_1$ and $E_2$ are not much different in value and when the interaction terms between $\psi_1$ and $\psi_2$ are large, it is found that the function giving the best approximation to the eigenfunction for the normal state of the system is neither $\psi_1$ nor $\psi_2$, but the combination of them, with the coefficients $a$ and $b$ of the same order of magnitude. In this case neither electronic formula alone can be assigned the molecule,

but instead both, with one perhaps more important than the other. The molecule could be described as fluctuating rapidly between the two electronic formulas, and achieving stability greater than that of either formula through the "resonance energy" of this fluctuation.

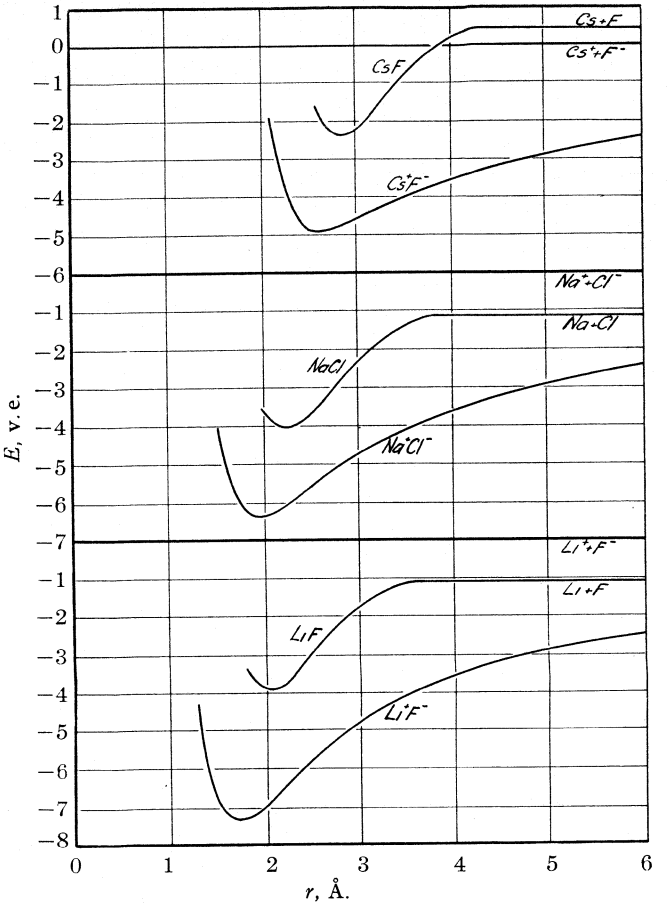



Fig. 5.—Potential energy curves for alkali halide molecules. The upper curve of each pair corresponds to electron-pair bond formation (Cs:F: , etc.), the lower to an ionic structure ($Cs^+F^-$, etc.).

It is impossible to carry out this program of directly evaluating the energy integral except in the simplest cases; but rough energy curves for various electronic structures can often be constructed by semi-empirical methods, and the discussion outlined above carried out with them. Thus information regarding the repulsive forces between ions obtained from the observed properties of ionic crystals can be used for ionic states of mole-

cules. In Fig. 5 the lower curve of each pair represents the electronic energy as a function of the internuclear separation for extreme ionic molecules CsF, NaCl and LiF. The attractive potential is taken as the Coulomb potential $-e^2/r$, polarization being neglected. (Polarization might lower the minimum of each curve by 1 or 2 v. e.) The repulsive potential used is $b/r^9$, with $b$ given the values which lead to the observed equilibrium separations in the crystals. The upper curves, which represent shared-electron-pair structures Cs : $\ddot{\text{F}}$ :, etc., are Morse curves with a dissociation energy of about 3 v. e., a value found to be correct to within ±1 v. e. for most electron-pair bonds. The relative positions of the curves are determined by ionization potentials and electron affinities.[15] It is seen that the ionic structures are much more stable than the electron-pair bond structures, so that the normal states of these alkali halide molecules (and presumably of the others) can be described as essentially ionic. There is, no doubt, some contribution of the electron-pair bond structure to the function $a\psi_{\text{ionic}} + b\psi_{\text{electron-pair}}$ which best approximates the normal state; but the coefficient $b$ is small compared with $a$, which is nearly unity.

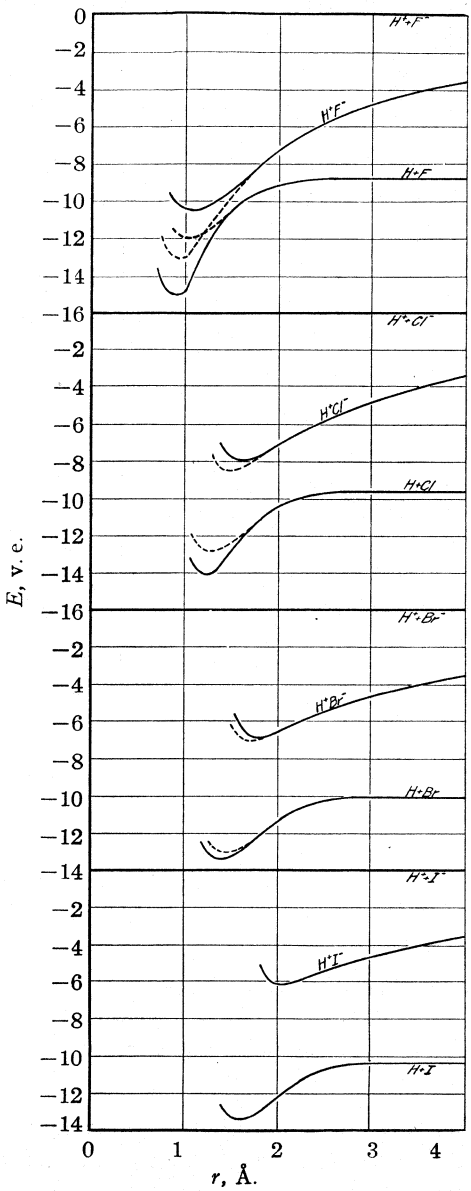



Fig. 6.—Potential energy curves for hydrogen halide molecules.

In Fig. 6 similar curves are shown for the hydrogen halide molecules. The electron-pair bond structures H : $\ddot{\text{F}}$ :, etc., are

[15] The values used are from a paper by Mr. J. Sherman, which will appear early in 1932 in *Chemical Reviews*.

represented by Morse curves of about 3 v. e. dissociation energy, with their minima at distances given by electron-pair bond radii.[16] The ionic curves were calculated with the use of hydrogen-like eigenfunctions, as described in a previous paper.[4] The screening constants used are from the revised set.[5] Polarization has been neglected.

It is seen that for hydrogen fluoride the two curves intersect, the minimum for the ionic curve lying below the other. In the region around $r = 1$ Å. the interaction between the two assumed structures would be large, and the resonance energy would be expected to amount to 1 or 2 v. e. A potential curve representing the normal state has been drawn in, corresponding to a combination of the ionic and electron-pair bond structures. The curve is drawn so that the minimum lies at the observed equilibrium separation of the nuclei, and at the energy level given by thermochemical data. An excited state also formed by combining the two original structures is shown.[17] In the eigenfunction $a\,\psi_{\text{ionic}} + b\,\psi_{\text{electron-pair}}$ approximating that of the normal state, the coefficients $a$ and $b$ are of the same order of magnitude, with $a$ somewhat larger than $b$. The normal HF molecule is represented by neither the formula $H^+F^-$ nor $H:\ddot{\underset{\cdot\cdot}{F}}:$, but by both, with $H^+F^-$ somewhat more important than $H:\ddot{\underset{\cdot\cdot}{F}}:$. The bond is largely ionic.

The curves for HCl, HBr and HI do not cross, in the main because the ionic radii of $Cl^-$, $Br^-$ and $I^-$ are much larger than that of $F^-$. Accordingly the normal states of these molecules are essentially of the electron-pair bond type, and the formulas $H:\ddot{\underset{\cdot\cdot}{Cl}}:$, $H:\ddot{\underset{\cdot\cdot}{Br}}:$, and $H:\ddot{\underset{\cdot\cdot}{I}}:$ may be used as giving a reasonably accurate picture of the state of the molecules. This conclusion had been reached before on the basis of other arguments, especially the tendency of fluorine alone of the halogens to form hydrogen bonds.

There is no doubt some interaction of the two structures for these molecules also, changing the curves by a small amount, as indicated for HCl and HBr.

It is not possible at the present time to carry out similar calculations for more complicated molecules, inasmuch as a small change in internuclear distance produces a very large change in the Coulomb energy of highly charged ions, and the equilibrium distances cannot yet be accurately predicted. Certain less specific conclusions can, however, be drawn. For example, the energy curves for a number of structures of $SiF_4$ (the pure ionic $Si^{4+}F^-_4$, and those with one, two, three or four fluorine atoms attached by electron-pair bonds) are found to have their minima

[16] Taken from a set contained in a paper by Linus Pauling and M. L. Huggins, to appear in *Z. Krist.*

[17] The values of $a$ and $b$ for this state must be such as to make the function orthogonal to that of the normal state.

close together. Neither the ionic extreme $Si^{4+}F^{-}_{4}$ nor the electron-pair bond extreme  represents the actual normal state of the molecule, which instead lies somewhere between them. There is little evidence as to which extreme is approached more closely. A tetrahedral configuration would be expected in either case.

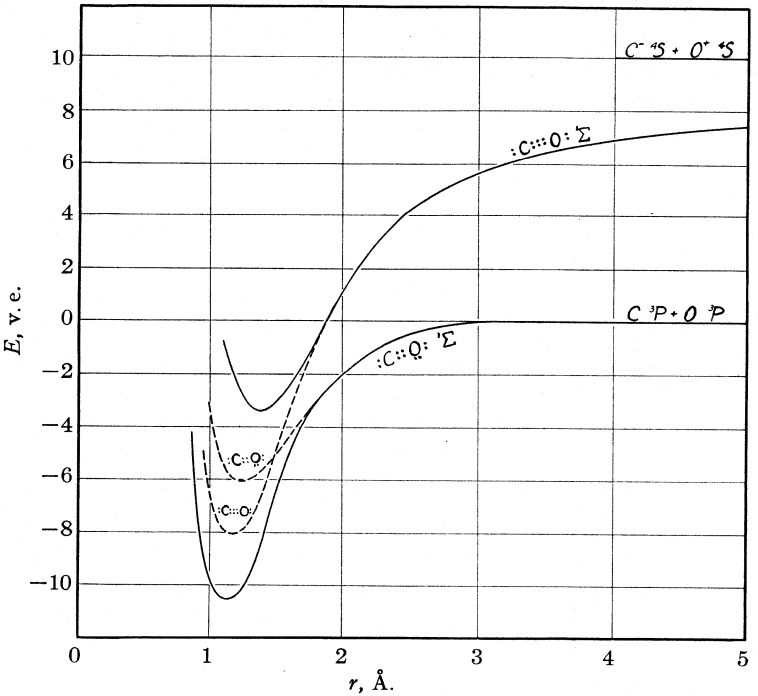



Fig. 7.—Potential energy curves for the carbon monoxide molecule.

Silica, the silicates and, in general, crystals containing oxygen or fluorine and metal atoms which can form noble-gas type cations are found to satisfy the electrostatic valence rule and the other rules for ionic crystals, which indicates that the ionic character of these substances is of greatest importance. The sulfides of metals other than the alkalies and alkaline earths, on the other hand, do not satisfy these rules; magnetic evidence further shows these substances not to be ionic.

The discussion of electronic energy curves also throws light on such questions as the structure of the carbon monoxide molecule. The empirical study of potential curves obtained from band spectral data has shown[18] that for atoms in the first row of the periodic system a double bond leads

[18] An account of this work will be published at some future time.

to a dissociation energy of about 6 v. e. and a triple bond to 9 v. e. In Fig. 7 the Morse curve due to normal atoms $C^3P$ and $O^3P$, extended by dashes to the left, corresponds to the double-bonded structure :C::Ö:. The upper curve with its dashed extension corresponds to the structure :C:::O:, formed from the ions $C^-\ ^4S$ and $O^+\ ^4S$. In drawing this curve a Coulomb curve for large $r$ was combined with a 9 v. e. Morse curve for small $r$ in such a way as to make the total dissociation energy 9 v. e. plus $\frac{e^2}{r_0}\left(1-\frac{1}{n}\right)$, with $n$ placed equal to 5 and $r_0$ to 1.25 Å. The electron affinity of carbon was estimated at 3.5 v. e.

It is evident that the normal state of CO is not the double-bonded state, especially since the normal molecule is found experimentally to lie 10.3 v. e. (rather than 6 v. e.) below the normal atoms. The triple-bonded ionic structure leads to a curve which crosses the other, dropping to about −8 v. e. Strong interaction between these two $^1\Sigma$ structures is to be expected for small values of $r$, giving rise to combined states represented by the two potential curves drawn in the figure. The normal state of CO is accordingly a combination of :C::Ö: and :C:::O:, with the latter of greater importance. On separating the nuclei the electronic structure changes, until from about 2 Å. on the double-bonded structure alone is present.[19]

## The Magnetic Criterion[12b]

Many compounds of transition elements behave differently from the substances discussed above, for the reason that the lowest ionic state and the lowest electron-pair bond state may contain different numbers of unpaired electrons, so that they cannot be combined with one another. An octahedral complex $[FeX_6]^{\equiv}$ forms a good example. If the complex contained extreme ionic bonds, the singlet ions $X^-$ and the $Fe^{+++}$ ion (with a stable state of maximum multiplicity, in accordance with the rules of line spectra) would produce a $^6\Sigma$ complex, containing five unpaired electrons, as shown in Fig. 4. An unstable ionic $^2\Sigma$ state would also be formed by pairing four of the electrons; it would lie several volt-electrons above the normal state. With extreme electron-pair bonds the normal state, involving $3d^2\ 4s\ 4p^3$ bond eigenfunctions, would be a $^2\Sigma$ state. A $^6\Sigma$ state, with the much less stable $4s\ 4p^3\ 4d^2$ bonds, would lie much higher. The energy levels of an actual complex would lie somewhere on the curves shown in Fig. 8. The normal state would be either $^2\Sigma$, mainly the octahedral electron-pair bond state with a small contribu-

[19] The arguments for the triple-bonded ionic structure presented by N. V. Sidgwick [*Chem. Rev.*, **9**, 77 (1931)] in the main support this structure also. Thus we may expect for :C::Ö: an electric moment with oxygen negative, for :C:::O: one with oxygen positive (the electronic structure being symmetrical, and oxygen having the larger nuclear charge), so that the combined structure could well lead to the observed very small electric moment.

tion from the excited ionic extreme, or $^6\Sigma$, mainly ionic with a small contribution from the excited electron-pair bond extreme. It is accordingly convenient to designate the $^2\Sigma$ state as essentially of the electron-pair bond type, and the $^6\Sigma$ state as essentially ionic, and to take the intersection of the two curves as a discontinuity in the normal state.

The multiplicity can be determined from the experimental values of the magnetic susceptibility, the magnetic moment in Bohr magnetons being equal to $2\sqrt{S(S+1)}$, in which $S$ is the spin quantum number. (The multiplicity is $2S + 1$.) The moments for $^2\Sigma$ and $^6\Sigma$ are 1.73 and 5.91, respectively. The experimental values for $K_3Fe(CN)_6$ and $(NH_4)_3FeF_6$ are 2.0 and 5.88, respectively, so that the bonds in the $[Fe(CN)_6]^{\equiv}$ ion are electron-pair bonds, and those in $[FeF_6]^{\equiv}$ are ionic.

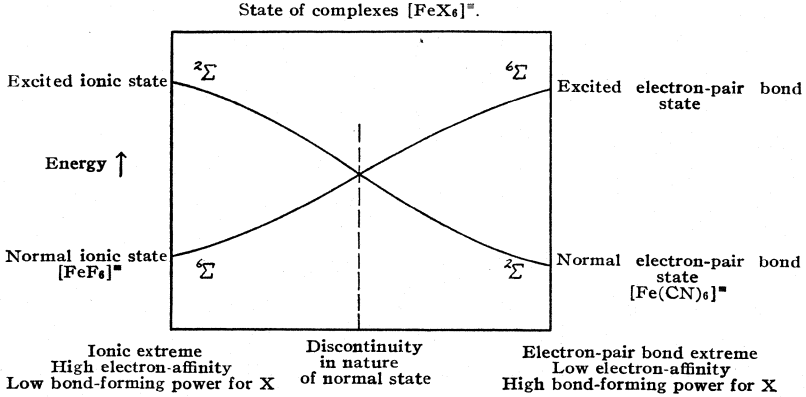



Fig. 8.—Diagram of two energy levels for complexes $[FeX_6]^{\equiv}$, showing an effective discontinuity in the normal state.

The magnetic criterion is particularly valuable because it provides a basis for differentiating sharply between essentially ionic and essentially electron-pair bonds. Experimental data have as yet been obtained for only a few of the interesting compounds, but these indicate that oxides and fluorides of most metals are ionic. Electron-pair bonds are formed by most of the transition elements with sulfur, selenium, tellurium, phosphorus, arsenic and antimony, as in the sulfide minerals (pyrite, molybdenite, skutterudite, etc.). The halogens other than fluorine form electron-pair bonds with metals of the palladium and platinum groups and sometimes, but not always, with iron-group metals.

## Summary

After a discussion of the properties of substances containing ionic bonds and electron-pair bonds, it is shown that the transition from one extreme bond type to another could take place continuously in some cases (when

the normal states for the two extremes have the same number of unpaired electrons), and not in others. A method of treatment of bond type based on electronic energy curves is developed. Its application shows the normal alkali halide molecules to be essentially ionic. HF is largely ionic, while HCl, HBr and HI contain electron-pair bonds. The normal state of CO corresponds to both structures :C::Ö: and :C:::O:, with the latter predominant. Some general statements based on observed magnetic moments are made relative to the types of bonds formed by metals of the transition groups.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 298]

# EXPERIMENTS ON THE RATE OF DISSOCIATION OF NITROGEN TETROXIDE

BY PHILIP D. BRASS AND RICHARD C. TOLMAN

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**1. Previous Work.**—The dissociation of the colorless gas nitrogen tetroxide to form the highly colored red nitrogen dioxide has long been of interest to chemists. The equilibrium between the two gases provided one of the earliest examples for the application of thermodynamics to the calculation of the effect of temperature on chemical equilibrium;[1] and the very high rate of attainment of the equilibrium has been the subject of much speculation and experiment.

Previous to the quite different mode of attack to be described in the present article, a number of attempts have been made to determine the rate of the dissociation and recombination by measuring the velocity of sound through an equilibrium mixture of the two gases. Using high enough frequencies, one should obtain the velocity corresponding to the passage of the sound wave through the mixture of the two gases without reaction, but at low enough frequencies one should expect the equilibrium to adjust itself by reaction to the periodic compression and rarefaction, and hence should expect a decrease in the velocity of sound, which amounts theoretically to about 3.8% with gas at 25° and atmospheric pressure.[2] At intermediate frequencies one should expect a "critical region" with intermediate velocities. A theory of the effect of frequency on the velocity

[1] Gibbs, *Trans. Connecticut Acad.*, **3**, 108, 343 (1875-6-7-8); *Am. J. Sci.*, Ser. 3, **18** (1879).

[2] See Table VII in article by Grüneisen and Goens.[8] Their calculation was made in accordance with the theory of Einstein,[3] correcting for an obvious slip as to sign in Einstein's work. Kistiakowsky and Richards,[10] apparently not correcting for the wrong sign, give a larger theoretical lowering of about 5.1%.

of sound in such a gas, assuming that the absorption coefficient is sufficiently small, has been developed by Einstein.[3]

Using frequencies in the audible range, measurements of the velocity of sound through the mixture have been made by E. and L. Natanson,[4] Keutel,[5] Argo,[6] Selle[7] and Grüneisen and Goens.[8] E. and L. Natanson measured the velocity for only a single frequency, and hence could make no estimate as to the position of the critical range of frequencies where the velocity would be affected by the reaction. Keutel and also Selle came to the conclusion that the critical range lay within the audible. However, the experiments of Argo and the very thorough and careful investigation of Grüneisen and Goens make it appear certain that the critical range lies above the audible range of frequency, say 15,000 cycles per second, and that the specific reaction rate for the dissociation of nitrogen tetroxide at 760 mm. pressure and 25°, assuming first order decomposition, is at least as high as $10^4$ seconds$^{-1}$.

Using frequencies in the ultrasonic range, measurements have been made by Olson and Teeter[9] and by Kistiakowsky and Richards.[10] Olson and Teeter concluded that the critical range had actually been passed at a frequency of 51,570 cycles per second in gas at 565 mm. pressure and 25°. The more extensive work of Kistiakowsky and Richards, however, now makes it appear reasonably certain that the critical range lies above 80,000 cycles per second at pressures from 300 to 760 mm. at 25°, and that the specific rate for the reaction is at least as high as $5 \times 10^4$ seconds$^{-1}$.

**2. Criticism of the Acoustic Method.**—There are a number of serious difficulties inherent in the acoustic method, owing primarily to the very small change in velocity that would be expected theoretically under the two assumptions of no reaction and a complete adjustment of the equilibrium to the periodic changes in pressure.

The apparatus for making the measurements is complicated, and the possible effect of the walls of the tube containing the gas must be allowed for. Small traces of impurities are known to have a large effect on the velocity; thus with the most careful purification Kistiakowsky and Richards were not able to duplicate results with successive fillings to better than about one-half a per cent.

A particularly serious difficulty also lies in the fact that the velocity of sound appears to vary with the frequency, when this is pushed high

[3] Einstein, *Berlin. Ber.*, 380 (1920).
[4] E. and L. Natanson, *Wied. Ann.*, **24,** 454 (1885); **27,** 606 (1886).
[5] F. Keutel, Inaug.-Diss., Berlin, 1910.
[6] W. L. Argo, *J. Phys. Chem.*, **18,** 438 (1914).
[7] H. Selle, *Z. physik. Chem.*, **104,** 1 (1923).
[8] E. Grüneisen and E. Goens, *Ann. Physik*, **72,** 193 (1923).
[9] A. R. Olson and C. E. Teeter, Jr., *Nature*, **124,** 444 (1929).
[10] G. B. Kistiakowsky and W. T. Richards, THIS JOURNAL, **52,** 4661 (1930).

enough, even in a pure non-reacting gas,[11] although much work must still be done in this field.

The absorption of sound by the gas, which increases greatly with decreased pressure,[12] and would probably increase with frequency at high enough frequencies,[13] is also serious, since it would otherwise be advantageous to work at lower pressures and temperatures in order to slow down the rate of the reaction, and at higher frequencies in order to get up into the critical region. With increased absorption the accuracy of the measurements is decreased, and the validity of the Einstein theory brought into question.

Finally it may be remarked that the method is in any case an indirect one, and that, up to the present time at least, no actual reaction velocity has ever been measured by this method, nor indeed any effect of reaction on the velocity of sound experimentally demonstrated.

**3. General Nature of the Present Experiments.**—The above well-known difficulties with the acoustic method make it desirable to investigate the possibility of other methods. In the present article we shall describe an entirely different mode of attack which, in spite of its own serious difficulties and uncertainties, nevertheless appears to give some idea as to the rate of dissociation of nitrogen tetroxide.

The general nature of the method was to cause an equilibrium mixture of the two gases to flow with a sudden drop in pressure through a perforated diaphragm, and take measurements of the temperature of the gas both before passage through the diaphragm and at successive positions in the path of flow beyond. The sudden drop in pressure and concentration on passage through the diaphragm should be followed by an increase in the degree of dissociation of the tetroxide and, since the reaction is endothermal, this should be accompanied by a drop in the temperature of the gas. Hence, knowing the velocity of flow and the temperature at different distances beyond the diaphragm, it was hoped that conclusions as to the rate of dissociation could be drawn.

The interpretation of the results obtained by the method is affected by two serious sources of uncertainty which must now be mentioned. They will be considered in more detail later.

The first uncertainty arises because of lack of knowledge as to the behavior of the jets which issue from the fine holes in the diaphragm. We purposely used a large number of fine holes set close together to try to break up the persistence of any jet structure, and we shall make our calculations on the assumption that we had a flow of homogeneous gas. We cannot be certain, however, how well this was actually achieved.

[11] G. W. Pierce, *Proc. Am. Acad.*, **60**, 271 (1925); C. D. Reid, *Phys. Rev.*, **35**, 814 (1930).

[12] See Ref. 10, Table VII.

[13] See Ref. 11, first article, section 26.

The second uncertainty arises because of difficulties in determining the temperature of the flowing gas. The measurements were made with the help of copper–constantan thermocouples inserted in the path of the gas flow, as will be described later in detail. The exact interpretation of the readings is made difficult, (a) because the metal of the thermocouples might exert a catalytic influence on the dissociation, (b) because the actual readings obtained presumably correspond to a combined effect partly coming from the walls and only partly from the gas, and (c) because the rapidly flowing stream of gas in impinging on the thermocouples will tend to heat up by friction and compression. With regard to the possibility of catalytic influence, we have no evidence. With regard to the second difficulty of conduction of heat from the walls to the thermocouple junctions, however, it should be noted that the walls tend to some extent to drop to the same temperature as the adjacent gas, and that the difference in temperature between successive thermocouples, which is the thing of prime interest, is presumably more correctly given by the readings than the absolute temperatures. With regard to the possible heating of the thermocouples by the friction and compression of the impinging gas, it may be noted that this would also tend to some extent to balance out in the case of the temperature differences between successive couples, and in addition it may be remarked that the kinetic energy of the gas would not be high enough to produce an important effect of this kind, if the conditions of homogeneous flow assumed for our calculations are really correct. Finally, considerable insight into the significance of the observed temperature readings was obtained by carrying out *blank runs* with a non-dissociating gas, ethyl chloride, and comparing the readings with those obtained in the *regular runs* with the nitrogen tetroxide.

In spite of the above uncertainties the results obtained with the method are of considerable interest, especially in view of the negative results obtained with the acoustic method, and we may now proceed to a detailed description of the apparatus.

**4. Description of the Apparatus.**—The apparatus consisted essentially of a boiler B, containing liquid tetroxide and delivering gas through the diaphragm D, which then passed down the flow tube T and was finally condensed at C with the help of liquid air in a Dewar tube, as shown in Fig. 1.

The boiler B, which was about 9 cm. in diameter and 22 cm. in length, was made of Pyrex glass and arranged to accommodate the electrical heater H as shown in the figure. This was found to assure smooth boiling. The side tube $M_1$ led to a manometer for measuring the high pressure before passage through the diaphragm, and also provided connection for filling the apparatus, pumping, and attaching phosphorus pentoxide tubes when desired.

The boiler was connected with a barrel, ground to receive a plug carrying the diaphragm, as shown in detail in Fig. 2. The plug P was made of lead glass in order that the platinum diaphragm could be sealed to it. It was provided with a thermocouple T for measuring the temperature of the gas before passage through the diaphragm.

The diaphragm D was a platinum disk 0.127 mm. thick with a turned-over lip which fitted inside the plug for sealing. It was provided with 96 holes so distributed that equal areas of the disk contained approximately equal numbers of holes. They were made by forcing the point of a needle a set distance through the disk in the direction opposite to that of the flow, and had a diameter varying from 0.08 to 0.12 mm. with an average of 0.10 mm.

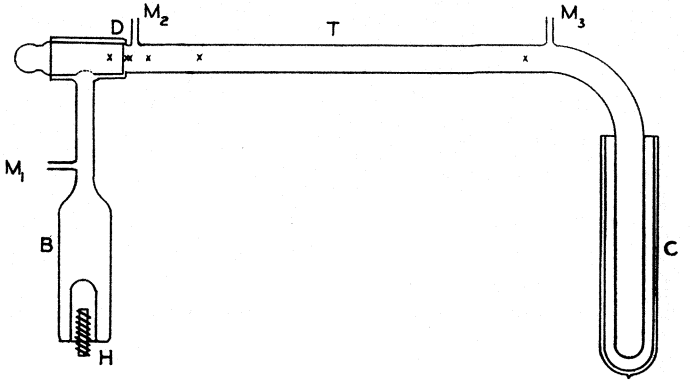


Fig. 1.—General view of apparatus. Crosses indicate position of thermocouples.

The barrel B was connected to the flow tube by a square shoulder, arranged so that the holes in the diaphragm were approximately uniformly distributed over the open area provided. The ground glass joint between the plug and barrel was made tight by painting on the outside with "Duco."

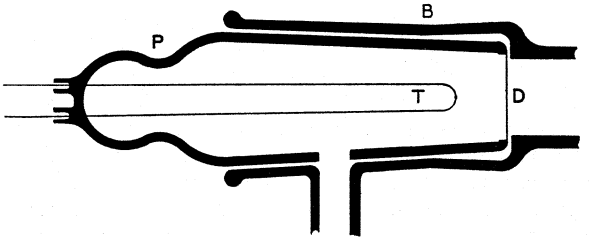


Fig. 2.—Detail of plug and diaphragm.

The flow tube was made from a uniform piece of Pyrex tubing having an inside diameter of about 4 cm. and a total length of 120 cm., with a smooth right-angle bend 75 cm. from the diaphragm. It was provided with manometer connections at $M_2$ as close as possible to the diaphragm and at $M_3$ 60 cm. further down the tube. The tube was also provided with thermocouples as will be described below. There were three manometers: manometer no. 1, for measuring the high pressure before passage through the diaphragm, was an ordinary U-tube filled with mercury open at one end to the atmosphere, and connected at the other end either directly to the boiler at $M_1$ in the case of the blank runs, or through another U-tube filled with concentrated sulfuric acid for protection against the nitrogen oxides in the case of regular runs. Even with this protection the mercury was attacked in a short time and the tube had to be cleaned frequently. Manometer No. 2, for measuring the pressure drop in the flow tube, was

merely a U-tube filled with mercury in the case of the blank runs and sulfuric acid in the case of the regular runs, and connected between $M_2$ and $M_3$. Manometer No. 3, for measuring the absolute value of the pressure on the low side of the diaphragm, was similar to No. 1 in the blank runs, and consisted of a closed-end U filled with sulfuric acid in the case of the regular runs. It was connected to the tube at $M_3$.

Thermocouples were placed, in the high pressure gas as already shown in Figs. 1 and 2, at successive positions along the flow tube as approximately shown by the crosses in Fig. 1, and also in a water-bath contained in a Dewar tube to give a base-point for the temperature measurements.

The thermocouples were led into the flow tube through insets as shown in Fig. 3. The leads were sealed through lead glass plugs which were ground to fit into Pyrex sockets sealed to the flow tube. "Duco" was used on the outside to prevent leaks around the lead wires and the ground-glass joints. The wires were prevented from coming in contact, by insulating one of them with a fine glass tube, not shown in the figure, running from the seal to a point between the end of the plug and the entrance to the flow tube. Care was taken to minimize the contact between the wires and the glass walls, and the wires were run two-thirds to three-quarters of the way across the tube at right angles to the flow, so as to give the best conditions for indicating the temperature of the gas at the particular distance down the flow tube involved.

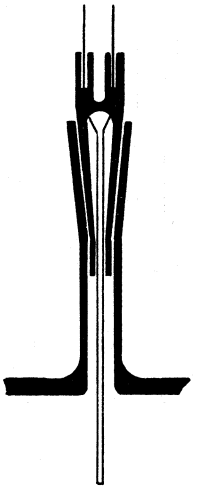

Fig. 3.—Detail of thermocouples.

The thermocouples were constructed of copper and constantan joined together with soft solder. They were attacked only slowly by the nitrogen oxides, were inexpensive, had high sensitivity, and since one of the metals was copper made it possible to have no junctions between unlike metals except at the points whose temperature difference was desired.

The electrical connections were made as follows. All the constantan wires were soldered together outside the tube, and each copper wire went to a switchboard so arranged that any desired pair of thermocouples could be thrown in opposition on to the galvanometer. No attempt was made to balance the e. m. f., owing to the necessity for rapidity in making the measurements, but direct readings of the galvanometer deflections were taken. Two galvanometers of different sensitivities were provided for measuring large and small temperature differences.

For some of the experiments the flow tube from the diaphragm to the bend was enclosed in a metal tank which could be used as an air or water thermostat for controlling the external temperature.

**5. Experimental Method.**—The nitrogen tetroxide used in the regular runs was either prepared by heating lead nitrate or taken from a cylinder furnished through the courtesy of the Fixed Nitrogen Research Laboratory. The latter material contained some nitric oxide which was removed by treating with oxygen. It should be especially noted that material of extreme purity is not necessary for these experiments as in the case of the acoustic method. The material used was always dried by standing over phosphorus pentoxide and in some cases a drying tube was sealed on to the apparatus in which the material was condensed when not in use. No special correlation between the results and the extent of drying was apparent.

The ethyl chloride used in the blank runs was of U.S. P. grade as sold to physicians for local anesthesia. It was chosen as a comparison substance since its boiling point (12.5°) is nearer to that of nitrogen tetroxide (21.6°) than any other common, non-poisonous, stable liquid.

The apparatus was filled by condensing the desired material at C, Fig. 1, with the help of liquid air, and was then pumped off, the residual air being flushed out by warming up the tetroxide. It was necessary to remove the residual air thoroughly in order to obtain low pressures in the flow tube when running.

Four operators were needed to carry out a run. One man adjusted the heating of the boiler to maintain a prearranged pressure of gas on the high side of the diaphragm, and took readings of the three manometers at thirty-second intervals and thermostat temperatures when the bath surrounding the flow tube was used. A second man maintained the liquid air level in the Dewar so as to obtain the maximum rate of condensation. A third man took galvanometer readings corresponding to different pairs of thermocouples in a prearranged order. These readings were taken at ten-second intervals. The fourth man called the time for the readings and recorded results. The total time for a run was from 450 to 900 seconds according to conditions.

**6. Experimental Results.**—Using the apparatus and method described above, eighteen regular runs were made using nitrogen tetroxide and nineteen blank runs using ethyl chloride. In nine of the regular runs the flow tube was either in the open air at room temperature or surrounded by an air thermostat at room temperature, and in the remaining nine the flow tube was surrounded by water at room temperature. In seven of the blank runs the flow tube was surrounded by air at approximately room temperature, in four runs by air at an elevated temperature, and in eight runs by water at an elevated temperature.

The nine regular runs in which the flow tube was surrounded by water gave very irreproducible results, and the eight blank runs in which the flow tube was surrounded by water at an elevated temperature showed that the thermocouple readings were much more affected by the temperature of the surroundings with water in the thermostat than with air. Owing to this irreproducibility and to the fact that our interest lies in the temperatures which would be obtained under adiabatic conditions, we shall consider in detail only the data obtained when the flow tube was surrounded by air.

These results are summarized in Tables I, II and III, arranged according to the material used and the approximate temperature ranges for the air surrounding the flow tube. The first column of the tables gives the number of the run in chronological order. The second and third columns give the pressures of the gas before and after passage through the diaphragm. The remaining columns give the calculated temperature intervals between successive thermocouples in the line of flow.

The nature of the results is also shown in Fig. 4, where the calculated temperatures of the thermocouples are plotted against position for runs 1 and 2, illustrating the behavior of nitrogen tetroxide expanded into the flow tube surrounded by air at room temperature, and for runs 9 and 15, illustrating the behavior of ethyl chloride expanded from about the same pressure, in one case into the flow tube surrounded by air at room temperature, and in the other case into the flow tube surrounded by air at

TABLE I

REGULAR RUNS WITH NITROGEN TETROXIDE

Temp. of gas arriving at diaphragm.....23–28°
Temp. of air surrounding flow tube.....22–24°

| Run | High press., mm. | Low press., mm. | Temperature differences, °C. 1–2 | 2–3 | 3–4 | 4–4a | 4(4a)–5 | 5–6 |
|---|---|---|---|---|---|---|---|---|
| 5 | 720 | 7 | −31.0 | −2.4 | −1.6 | | +0.4 | +7.9 |
| 6 | 710 | 9 | −31.0 | −2.0 | −1.5 | | +0.3 | ... |
| 14 | (500) | 9 | −29.4 | −0.3 | −1.0 | −0.1 | +1.3 | +6.0 |
| 1 | 485 | 6 | −29.1 | −2.3 | −1.0 | | −0.1 | +5.2 |
| 2 | 485 | 4 | −27.9 | −2.1 | −0.5 | | +0.2 | +7.4 |
| 3 | 300 | 6 | −23.6 | −1.5 | 0.0 | | +1.9 | +9.7 |
| 4 | 300 | 8 | −22.2 | −0.6 | −0.2 | | +1.6 | +7.3 |
| 7 | 300 | 10 | −23.0 | −0.8 | −0.7 | | +0.8 | +9.5 |
| 8 | (300) | 8 | −23.5 | −1.1 | −1.2 | | +1.1 | +8.1 |

TABLE II

BLANK RUNS WITH ETHYL CHLORIDE

Temp. of gas arriving at diaphragm.....22–28°
Temp. of air surrounding flow tube.....22–27°

| Run | High press., mm. | Low press., mm. | Temperature differences, °C. 1–2 | 2–3 | 3–4 | 4–4a | 4(4a)–5 | 5–6 |
|---|---|---|---|---|---|---|---|---|
| 19 | 560 | 18 | −3.2 | +0.2 | −0.1 | 0.0 | +0.1 | −0.4 |
| 20 | 560 | 16 | −2.5 | +0.4 | +0.1 | 0.0 | +0.2 | +0.4 |
| 11 | 490 | 41 | −2.4 | +0.2 | 0.0 | | −0.4 | +0.3 |
| 10 | 475 | 38 | −3.4 | +0.3 | −0.2 | | −0.1 | −0.2 |
| 9 | 470 | 41 | −3.2 | +0.3 | −0.6 | | −0.6 | +0.4 |
| 12 | 290 | 40 | −0.2 | +0.3 | +0.1 | | +0.6 | +0.8 |
| 13 | 290 | 52 | −0.5 | +0.2 | +0.1 | | +0.3 | +0.6 |

TABLE III

BLANK RUNS WITH ETHYL CHLORIDE

Temp. of gas arriving at diaphragm.....27–31°
Temp. of air surrounding flow tube.....40–44°

| Run | High press., mm. | Low press., mm. | Temperature differences, °C. 1–2 | 2–3 | 3–4 | 4–4a | 4a–5 | 5–6 |
|---|---|---|---|---|---|---|---|---|
| 17 | 690 | 3 | −1.2 | −1.3 | +3.3 | −0.1 | +4.2 | +2.4 |
| 15 | 560 | 9 | +1.1 | −1.6 | +2.7 | +0.2 | +3.9 | +2.4 |
| 16 | 560 | 25 | +1.6 | −1.4 | +2.4 | +0.2 | +3.9 | +2.8 |
| 18 | 295 | 10 | +5.0 | −2.3 | +2.7 | +0.6 | +5.3 | +1.6 |

an elevated temperature. Temperatures are plotted from the temperature of the high pressure gas as a starting point, and the distances are plotted from the position of the diaphragm as a starting point. Beyond the last point shown on the plots the temperature rises only slightly before reaching the final value given by the last thermocouple at approximately 60 cm. from the diaphragm.

The runs varied in length from six to twenty-five minutes according to the amount of material in the apparatus and the pressure of gas main-

tained on the high side of the diaphragm. Approximately steady conditions were obtained only in the middle of a run, and the data given in the tables are average values corresponding to readings taken from three minutes after the run started until one minute before all the material had passed over, or until the end of fifteen minutes in the case of very long runs.

The manometer readings for determining the pressures given in the second and third columns of the tables were taken every thirty seconds, but owing to difficulties with the manometers, which included the action of the oxides on the mercury even though it was protected by sulfuric acid, and the diffusion of the oxides through the sulfuric acid into the upper end of the closed manometer No. 3, the pressures recorded cannot be regarded as accurate. The pressures attained on the low side appeared to be very dependent on small amounts of residual permanent gas, which may have had a cushioning effect at the end of the flow tube where condensation took place. The actual rate of flow appeared mainly dependent on the pressure on the high side.

Galvanometer readings were taken every ten seconds, in general two successive readings on a given thermocouple in the case of the less sensitive galvanometer, and three to allow the more sensitive galvanometer to reach its final deflection. Only the final readings were used in making the averages, and this together with the large number of combinations read makes the number of readings included in the average for a given thermocouple small, varying from one to five. The temperature intervals given in the tables are calculated from the galvanometer readings from calibrations of copper–constantan couples.

Thermocouple No. 1 was located in the gas just before its passage through the diaphragm. The remaining thermocouples Nos. 2 to 6 were located at the approximate distances from the diaphragm of 4.5, 9.5, 35.5, 90 and 593 mm. in Runs Nos. 1 to 13, and 2, 7, 22, 30, 89 and 587 mm. in Runs Nos. 14 to 20. In these latter runs the thermocouples were made with heavier constantan wire than in the earlier and this was doubled to give additional stiffness.

**7. The Qualitative Nature of the Results.**—The general nature of the results is evident from the figures given in the tables.

From the similarity in the results obtained under similar conditions and the progressive changes with changed conditions, it is evident that the experimental findings show sufficient reproducibility to warrant consideration. The run showing the least satisfactory agreement with the others is No. 14 in Table I, which is the only one in that table obtained with the second set of heavier thermocouples. This may mean that these thermocouples were irregularly affected to a greater extent by external conditions than the finer ones. (The very irreproducible runs made with

the flow tube immersed in water mentioned above were also made with these thermocouples.)

The regular runs made with nitrogen tetroxide as shown in Table I are characterized by a large drop in the computed temperature on passing through the diaphragm, followed by a small continued drop in the first few centimeters of the flow tube, and a gradual rise further down the tube. The initial drop is presumably to be correlated partly with an ordinary Joule–Thomson effect but mainly with the heat used up by the dissociation of tetroxide, the small continued drop to be correlated with a continuation of the dissociation toward completion, and the final small rise with the heating effect of the walls of the tube. The runs show a smaller temperature drop the lower the initial pressure, and this is perhaps to be explained partly by the decreased change in degree of dissociation, and partly by the increased effect of the walls when a smaller amount of gas is flowing through the apparatus.

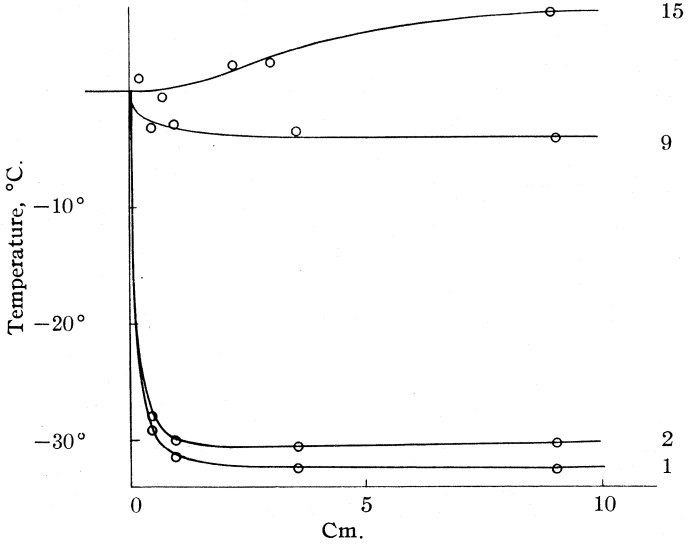


Fig. 4.—Plot of typical runs.

The blank runs made with ethyl chloride with the flow tube surrounded by *air at nearly the same temperature as the ethyl chloride* show a small initial drop in temperature in passing through the diaphragm, followed by small oscillations which have been neglected in drawing the curve in Fig. 4, and may be due to spurious causes. The small initial drop is perhaps to be correlated with the Joule–Thomson effect which amounts[14] to −4.51° per atmosphere drop in pressure at 20°. The initial drop is smaller the lower the initial pressure, and this is perhaps to be explained partly

[14] "International Critical Tables," Vol. V, p. 146.

by the decreased Joule–Thomson effect and partly by the increased effect of the walls when a smaller amount of gas is flowing through the apparatus.

The blank runs made with ethyl chloride with the flow tube surrounded by *air at an elevated temperature* show the effect of the walls in leading to higher temperature readings, with a gradual rise in passing down the tube and only the highest pressure run showing the initial drop which we have correlated above with the Joule–Thomson effect. The small oscillations in the readings may be due to spurious causes and have again been neglected in drawing the curve in Fig. 4.

The combined effect obtained by comparing the results obtained in the two kinds of blank runs with those obtained in the regular runs reinforces the impression that the temperature drops experienced by the nitrogen tetroxide in passing through the diaphragm and flowing down the tube are mainly to be correlated with the dissociation of the tetroxide which results from the decrease in its concentration.

**8. Quantitative Discussion of the Results.**—Although the results obtained are certainly not very accurate, and their interpretation is not unambiguous, nevertheless it seems desirable to use them for a preliminary calculation of the rate of dissociation of nitrogen tetroxide, since a knowledge of this very fast rate would be of importance for the theory of chemical kinetics, and the elaborate acoustic method has so far furnished no figure at all. The result which we calculate must, however, be regarded as subject to very great uncertainty, perhaps even as to order of magnitude.

(a) **Data for the Calculation.**—As data for the calculation we shall take the average of the results obtained in runs 1 and 2, which appeared to be typical and reasonably clean cut runs, made under nearly the same conditions and both of them taking the same total time for the material to pass over. The averaged data for the two runs are summarized in Table IV.

TABLE IV

AVERAGED DATA FOR RUNS 1–2

| | |
|---|---|
| Weight of $N_2O_4$ in apparatus, g. | 107 |
| Inside diameter of flow tube, cm. | 3.64 |
| Total time of flow, sec. | 690 |
| Pressure of gas at diaphragm, mm. | 485 |
| Pressure of gas leaving diaphragm, mm. | 5 |
| Temperature of gas arriving at diaphragm, °C. | 26.8 |
| Temperature at 0.45 cm. from diaphragm, °C. | −1.7 |
| Temperature at 0.95 cm. from diaphragm, °C. | −3.9 |
| Temperature at 3.55 cm. from diaphragm, °C. | −4.7 |
| Temperature at 9.0 cm. from diaphragm, °C. | −4.7 |
| Temperature at 59.3 cm. from diaphragm, °C. | +1.6 |

(b) **Corrected Temperatures.**—Before using the data given in Table IV, we must first consider two probable sources of error in the tempera-

ture measurements. The first of these lies in the fact that the gas is colder than the walls of the flow tube and hence presumably receives heat from them on its passage down the tube. The second lies in the fact that the thermocouple wires presumably conduct heat from the point where they pass through the walls down to the thermal junctions, which hence register a higher temperature than that of the gas itself.

To obtain an approximate correction for the first error we note that the measured temperature, after falling sharply in the first few centimeters of the flow tube, then rises a moderate amount from $-4.7$ to $1.6°$ in the relatively long distance of 50.3 cm. between the last two thermocouples. If we correlate this rise of $0.125°$ per cm. with the actual heating up of the gas, we can then obtain an approximate correction to the preceding thermocouple readings with the help of this ratio. Doing so we then obtain the corrected temperature readings given in Table V, with a roughly estimated lower limit at $-6.0°$.

TABLE V

CORRECTED TEMPERATURES FOR RUNS 1–2

| | |
|---|---|
| Temperature of gas arriving at diaphragm, °C. | 26.8 |
| Temperature at 0.45 cm. from diaphragm, °C. | −1.8 |
| Temperature at 0.95 cm. from diaphragm, °C. | −4.0 |
| Temperature at 3.55 cm. from diaphragm, °C. | −5.1 |
| Temperature at 9.0 cm. from diaphragm, °C. | −5.8 |
| Estimated lower limit, °C. | −6.0 |

To obtain a direct correction for the fact that all the thermocouples in the flow tube are probably reading too high, owing to the conduction of heat down through the wires from the walls, is not made possible by any data that we have obtained. If the method were further developed, this error could presumably be decreased by going to very fine thermocouple wire, and a direct experimental determination of the proper correction be made.

In the absence of a direct method of correcting for this error, we may proceed instead by calculating the drop in temperature that might theoretically be expected on expanding the tetroxide and comparing the result with the measured drop from 26.8 to $-6.0°$. To make such a calculation, which at best can only be rough, we shall assume that the heat of reaction $Q_p$ absorbed when one mole of tetroxide dissociates is a constant independent of pressure and temperature, and that the heat capacity $C_p$ of one mole of tetroxide is also a constant independent of pressure, temperature and the degree of dissociation of the tetroxide. For the drop in temperature we can then write the following expression, derivable from the first law of thermodynamics

$$(T - T_0) = (\alpha_0 - \alpha)\frac{Q_p}{C_p} \qquad (1)$$

where $T$ and $\alpha$ are the original temperature and degree of dissociation of the tetroxide before passage through the diaphragm and $T_0$ and $\alpha_0$ are the final values of these quantities. Furthermore, for the values of $\alpha$ and $\alpha_0$ we may use Schreber's[15] expression for Natanson's empirical determination of the equilibrium constant, which gives us the two further equations

$$\log \frac{4\alpha^2 p}{1 - \alpha^2} = -\frac{2866.2}{T} + \log T + 9.13242 \qquad (2)$$

and

$$\log \frac{4\alpha_0^2 p_0}{1 - \alpha_0^2} = -\frac{2866.2}{T_0} + \log T_0 + 9.13242 \qquad (3)$$

where $p$ and $p_0$ are the initial and final pressures in millimeters and the logarithms are to the base 10.

We thus have three equations for determining the three unknowns $T_0$, $\alpha$ and $\alpha_0$. For the known quantities we take the initial and final pressures and the initial temperatures from Table IV, and we take the ratio $Q_p$ over $C_p$ to be 1000, corresponding to the heat of reaction 13,600 cal. per mole[16] and an assumed constant heat capacity for a mole of partially dissociated tetroxide of 13.6 cal. per degree,[17] the calculated value of the final temperature $T_0$ being very insensitive to the value used for this ratio. Solving the equations by a method of approximation, we then obtain for the initial and final degrees of dissociation $\alpha = 0.2344$ and $\alpha_0 = 0.2812$, and for the final temperature $-19.5°$.

Since the result obtained is very dependent on the accuracy of Schreber's equation, and no allowance has been made for the true Joule–Thomson effect, the value $-19.5°$ cannot be regarded as very certain. It is nevertheless gratifying to find that the calculated drop from 26.8 to $-19.5°$ is not so very much greater than the measured drop from 26.8 to $-6.0°$, and the result confirms our interpretation of the drop as mainly due to the increased dissociation which occurs.

Since the actual final temperature is certainly less than the measured value of $-6.0°$, we shall make our further calculations of the rate of dissociation not only on the assumption that the final temperature is $-6°$, but also assuming $-13$ and $-20°$ for this quantity.

(c) **Theory of Reaction Rate Calculation.**—We must now consider the theory on which we shall base our calculation of the reaction rate from the rate at which the temperature is falling as the material is passing down the flow tube. At a given point in the flow tube let $v$ be the

[15] Schreber, *Z. physik. Chem.*, **24**, 651 (1897).

[16] Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923, p. 561.

[17] Compare with the measurements of McCollum, THIS JOURNAL, **49**, 28 (1927). and the estimates of Kistiakowsky and Richards, Ref. 10.

volume containing one mole of the partially dissociated tetroxide, and $\alpha$ be the actual degree of dissociation which it has attained, so that

$$C_1 = (1 - \alpha)/v \tag{4}$$

is the actual concentration of nitrogen tetroxide and

$$C_2 = 2\alpha/v \tag{5}$$

is the actual concentration of nitrogen dioxide at that point. Substituting into the familiar expression for rate of reaction

$$-\frac{dC_1}{dt} = k_1C_1 - k_2C_2^2 \tag{6}$$

we then obtain

$$\frac{d\alpha}{dt} = k_1(1 - \alpha) - k_2\frac{4\alpha^2}{v} \tag{7}$$

for the rate at which the degree of dissociation is increasing in terms of the specific reaction rates $k_1$ and $k_2$, for the forward and reverse reactions. On the other hand, if we let $K_c$ be the equilibrium constant for the reaction and $v_\epsilon$ and $\alpha_\epsilon$ be the volume and degree of dissociation which would obtain under equilibrium conditions with the pressure and temperature at the point in question, we may write from the well-known relation connecting the specific rates for the forward and reverse reactions

$$K_c = \frac{k_1}{k_2} = \frac{4\alpha_\epsilon^2}{(1 - \alpha_\epsilon)v_\epsilon} \tag{8}$$

and in addition

$$\frac{v_\epsilon}{v} = \frac{1 + \alpha_\epsilon}{1 + \alpha} \tag{9}$$

as a relation connecting the actual volume $v$ and the equilibrium volume $v_\epsilon$ at the given pressure and temperature. Combining (7), (8) and (9) and solving for $k_1$ we then easily obtain

$$k_1 = \frac{(1 + \alpha)\, d\alpha/dt}{1 - \alpha^2/\alpha_\epsilon^2} \tag{10}$$

or substituting

$$dl/dt = u \tag{11}$$

where $u$ is the velocity of flow down the tube, we can write as our equation for determining the specific rate of decomposition

$$k_1 = \frac{u(1 + \alpha)\, d\alpha/dl}{1 - \alpha^2/\alpha_\epsilon^2} \tag{12}$$

where $d\alpha/dl$ is the change in degree of dissociation with distance down the tube.

To use this equation we must determine $\alpha$ and $\alpha_\epsilon$ from the thermocouple temperatures as functions of the distance from the diaphragm. And we must have a value for the velocity of flow $u$.

To determine the value of the actual degree of dissociation, we may use our previous equation (1), which gives

$$(\alpha - \alpha_1) = (T_1 - T)\frac{C_p}{Q_p} \tag{13}$$

where $\alpha_1$ and $T_1$ are the known degree of dissociation and temperature of the gas before passage through the diaphragm, and $T$ is the temperature of the gas at the point of interest.

To obtain a value for the theoretical equilibrium degree of dissociation $\alpha_\epsilon$, it would not be safe to use any empirical formula for the equilibrium constant such as Schreber's, owing to the uncertainty in the formulas when extrapolated to the low temperatures involved, and even more owing to the uncertainty in the absolute magnitude of the lower temperature $T$ which we have discussed in section 8b above. We may, however, proceed satisfactorily as follows.

Using an equation similar to (13)

$$(\alpha_0 - \alpha_1) = (T_1 - T_0)\frac{C_p}{Q_p} \tag{14}$$

we may obtain a value for the final degree of dissociation $\alpha_0$ ultimately attained by the gas at its final temperature $T_0$. The desired degree of dissociation $\alpha_\epsilon$ will then differ only moderately from $\alpha_0$. To calculate $\alpha_\epsilon$ from $\alpha_0$, we may then write in accordance with well-known relations

$$K_T = \frac{4\alpha_\epsilon^2 p}{1 - \alpha_\epsilon^2} \tag{15}$$

and

$$K_0 = \frac{4\alpha_0^2 p}{1 - \alpha_0^2} \tag{16}$$

where $p$ is the pressure, and $K_T$ and $K_0$ are the values of the equilibrium constant $K_p$ at the temperature $T$ of interest and the final lowest temperature $T_0$, and by combination easily obtain

$$\log \frac{\alpha_\epsilon^2}{1 - \alpha_\epsilon^2} = \log \frac{\alpha_0^2}{1 - \alpha_0^2} + \log \frac{K_T}{K_0} \tag{17}$$

Moreover, the difference between the temperature of interest $T$ and the final temperature $T_0$ will be so small that we can now safely apply the integrated van't Hoff equation in its simplest form to determine the last term in (17) and write

$$\log \frac{\alpha_\epsilon^2}{1 - \alpha_\epsilon^2} = \log \frac{\alpha_0^2}{1 - \alpha_0^2} + \frac{Q_p(T - T_0)}{2.303\ RTT_0} \tag{18}$$

as the desired equation for calculating $\alpha_\epsilon$ in terms of $\alpha_0$.

Finally, to calculate the velocity of flow $u$ at the point of interest, we may evidently write

$$u = \frac{m}{M}(1 + \alpha)\frac{RT}{p}\frac{1}{\pi r^2 t} \tag{19}$$

where $m$ is the mass of gas passing down the tube in time $t$, $M$ the molecular weight of the tetroxide, $r$ the inside radius of the flow tube and the other quantities have their previous significance.

The expressions (12), (13), (14), (17) and (19) now provide all the theoretical apparatus that is necessary for a calculation of the specific rate of decomposition $k_1$ of the tetroxide.

(d) **Calculated Values of the Reaction Rate.**—Collecting the equations which are necessary for a calculation of the specific reaction rate, we can write with some simple modifications

$$k_1 = \frac{u(1 + \alpha)\, d\alpha/dl}{1 - \alpha^2/\alpha_\epsilon^2} \tag{12}$$

$$\alpha = \alpha_1 + (T_1 - T)\frac{C_p}{Q_p}; \quad \frac{d\alpha}{dl} = -\frac{C_p}{Q_p}\frac{dT}{dl} \tag{13}$$

$$\alpha_0 = \alpha_1 + (T_1 - T_0)\frac{C_p}{Q_p} \tag{14}$$

$$\log \frac{\alpha_\epsilon^2}{1 - \alpha_\epsilon^2} = \log \frac{\alpha_0^2}{1 - \alpha_0^2} + \frac{Q_p(T - T_0)}{2.303\, RTT_0} \tag{18}$$

$$u = \frac{m}{M}(1 + \alpha)\frac{RT}{p}\frac{1}{\pi r^2 t} \tag{19}$$

To obtain a satisfactory calculation of $k_1$ from these equations, it is evident that we must first determine the slope $dT/dl$ at a point on the curve of descending temperatures sufficiently above the final temperature $T_0$ so that $\alpha$ and $\alpha_\epsilon$ will not be too nearly equal, and at a point where the data are such as to give a reliable value for the slope. With these considerations in mind we have plotted the temperatures given in Table V as a function of the distance from the diaphragm, and chosen as a basis for the calculations a point on the curve at $-2.9°$ half-way between the temperatures of the first two thermocouples in the flow tube, taking the slope at this point as $-4.4°$ per cm., which is the average drop per cm. between the two thermocouples. It may be noted that the glass sockets for these two thermocouples were sealed to the flow-tube at the *same* distance from the diaphragm, and the thermocouples then bent to the desired positions.

With the value thus obtained for the slope we have then calculated $k_1$ from the data in Tables IV and V, together with $\alpha_1 = 0.2344$, which is the value given by Schreber's equation at 26.8° and 485 mm., and using $Q_p = 13{,}600$ and $Q_p/C_p = 1000$ as in section 8b. The result obtained is given in the first line in Table VI.

Since the correct value for $C_p$ is not known, we have then repeated the calculation, assuming $Q_p/C_p = 800$, which corresponds to a value of $C_p = 17$ cal. per degree instead of 13.6. The result is given in the second line of the table.

Since the final temperature $-6.0°$ depends on an uncertain extrapolation and from our plot of temperature against position seems possibly too high, the calculations have again been repeated, using $-5.5°$ as the final temperature. The result is given in the third line of the table.

Finally, since all the temperatures in the flow tube are presumably lower than what is given by the thermocouple readings, as already discussed in section 8b, the calculations have further been repeated, lowering all

the flow tube temperatures first 7° below the values in Table V and then 14° below these values. This last would make $T_0$ equal to −20°, which is close to the theoretical final temperature calculated in section 8b from Schreber's equation. The results are given in the last two lines of Table VI.

TABLE VI

CALCULATED VALUES FOR SPECIFIC RATE OF DECOMPOSITION $k_1$

| Assumptions for calculation | | $k_1$, sec.$^{-1}$ |
|---|---|---|
| Temperatures as in Table V | $Q_p/C_p = 1000$ | 15.1 |
| Temperatures as in Table V | $Q_p/C_p = 800$ | 18.9 |
| Final temperature −5.5 | $Q_p/C_p = 1000$ | 17.6 |
| Temperatures in flow tube lowered 7° | $Q_p/C_p = 1000$ | 14.4 |
| Temperatures in flow tube lowered 14° | $Q_p/C_p = 1000$ | 13.6 |

It is evident from the table that the calculated result is not greatly affected by moderate changes in the assumptions, and we may take $k_1 = 15$ sec.$^{-1}$ as a reasonable figure for the order of magnitude of the calculated specific rate of decomposition.

**9. Conclusion.**—We have thus obtained a quite definite figure, $k_1 = 15$ sec.$^{-1}$, for the specific rate of decomposition of nitrogen tetroxide at the low pressure and temperature in our flow tube. At higher pressures and temperatures, the specific rate would presumably be much greater. Assuming the reaction rate actually second order, as is perhaps probable, and taking the heat of activation the same as the heat of reaction at constant volume, 13,000 cal., we calculate at 1 atm. and 25°, $k_1 = 2.2 \times 10^4$, assuming the final temperature to have been −6° as given in Table V, $k_1 = 4.2 \times 10^4$, assuming a final temperature of −13°, and $k_1 = 8.2 \times 10^4$, assuming a final temperature of −20°. The last of these figures is perhaps the most justifiable estimate, and is not far from the lower limits set by Grüneisen and Goens and Kistiakowsky and Richards using the acoustic method.

Nevertheless, in spite of the reasonably definite result which we have thus obtained for the rate of decomposition of nitrogen tetroxide, it must be strongly emphasized that our considerations have completely neglected disturbing effects which might arise from a persistence of jets in the flow back of the diaphragm. Study of this question would be very important for the further development of the method, and in the absence of this study it would be unwise to make any undue claims for the reliability of the figures which we have presented. If jets do persist in the flow behind the diaphragm, it is possible that the actual rate might be considerably higher than we have calculated, both because the velocity in the jets would be higher than we have assumed, and because the gradual expansion of the jets as they pass down the tube would delay the attainment of final equilibrium.

In addition to a study and possible improvement in the conditions of flow back of the diaphragm, the further development of the method would also demand more reliable temperature measurements in the flowing gas. This could perhaps be achieved by using much finer thermocouple wire, sealed across the tube to provide the stiffness necessary to withstand the flow of gas.

In conclusion it may be remarked that the experiments which we have described are in any case of considerable interest, since they at least exhibit qualitatively a definite positive effect which can only be explained by a high rate of dissociation of nitrogen tetroxide, in contrast to the acoustic experiments which so far have led only to negative effects from which a high rate can be inferred.

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## NOTES

**A Simply Constructed Absolute Manometer.**—This note describes a manometer developed in this Laboratory which we believe is unique if not superior to the usual types. It possesses the following features: (1) it may be constructed in almost any chemical laboratory; (2) it is easily emptied and cleaned; (3) the readings are absolute; (4) at least fair accuracy may be obtained without "boiling out" with mercury.

The construction is obvious from the drawing. If a cathetometer is not used, a scale is to be fixed between or in back of the second and third tubes which comprise the manometer proper. With the system open there will be about 29 inches between the upper and lower levels, so enough extra length is necessary to care for oscillations of the column after opening the system. The short arm at the left should be slanted considerably for reasons discussed later. Fairly large tubing is preferable to the usual barometer tubing since the error due to differences in capillarity when the walls become slightly dirty is practically eliminated. Six millimeter tubing is not too large. The tubes accessory to the manometer may be smaller to conserve mercury.

**Mounting.**—A board serves well to hold the tubes, which may be secured by fine wires. The greater the distance between the manometer tubes the greater the error if they are not perpendicular. This is not true, of course, if a cathetometer is used.

**Filling.**—The instrument is ready for use when the levels are conveniently adjusted and the space T is void of air. Use the best mercury obtainable, place the mounted instrument horizontally with the left side downward, immerse tube A in the mercury and apply a gentle, easily controlled vacuum to the other end. By proper manipulation of the instru-

ment and vacuum the mercury will rise, completely filling the tube until a point near 4 is reached. Close the stopcock, disconnect the vacuum and bring the instrument slowly to a vertical position. Excess mercury in the short arm may be poured out easily if the stopcock plug is withdrawn.

Unless such a device is "boiled out" with mercury, adsorbed air on the glass will eventually collect in space T. It may be detected by tipping the manometer backward. If air is present a minute bubble will persist after the columns should have connected. This bubble may be removed as follows. Connect both ends of the manometer to the same vacuum system. With a slight reduction of pressure draw level 1 just to the stopcock, which is then closed. Tip the instrument to the left to a horizontal position as when filling. If level 4 was originally high enough relative to the volume of T, no air will be admitted around the last bend. Set the slope of the tubes so that the bubble will just rise and escape near 4. Increasing the vacuum and tapping will aid in moving the bubble. Any air trapped in the recesses of the stopcock will not get past the first bend. Leakage at the stopcock is prevented by having the same vacuum attached at both ends. If the mercury can be kept clean this apparatus can be used with increasing accuracy. For rough work where the mercury is quickly dirtied, cleaning is much easier than in the case of the closed type since cleaning fluid and the like can be drawn or poured through without the fussy technique required by the latter.

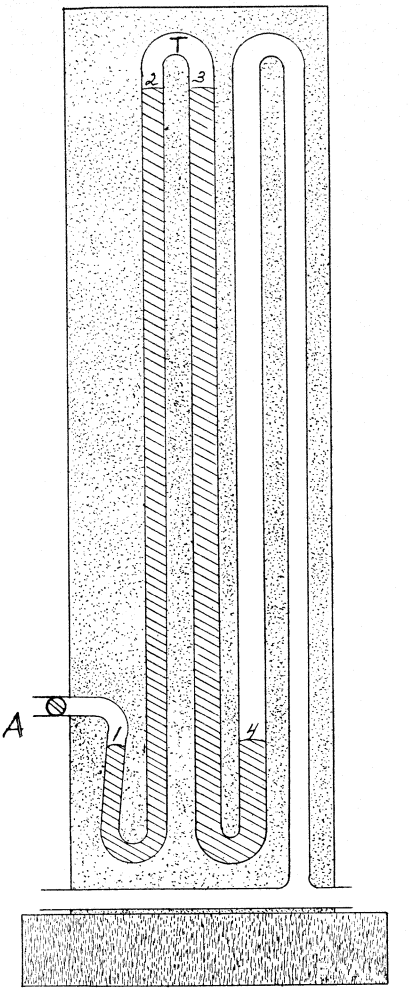


Fig. 1.

CONTRIBUTION FROM THE
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**Some Observations on Reactions between Certain Metallic Ions and the Ammonium Salt of Aurintricarboxylic Acid.**—Several years ago Hammett and Sottery[1] discovered that the ammonium salt of aurintricarboxylic acid could be used as a very sensitive reagent for the detection of aluminum. The new reagent is called "Aluminon." In acetic acid–acetate solution aluminum forms a bright red lake with this dye, which is fairly stable in ammonium hydroxide—ammonium carbonate solution. Observations on most of the common metallic ions, as well as silicic acid and phosphate, were made with this reagent. Ferric iron was the only one found to give a colored precipitate, the others either gave white precipitates or none at all. Iron, therefore, must be completely removed from the aluminum. This may be accomplished by co-precipitation of the iron with relatively large amounts of elements such as copper. Precipitation with sodium hydroxide, or sodium sulfide, followed by digestion for thirty to sixty minutes on a steam-bath, is satisfactory.

Middleton[2] reports that "Aluminon" forms lakes with the hydroxides or basic acetates of beryllium, cerium, erbium, lanthanum, neodymium, thorium, yttrium and zirconium. These lakes are deeper red than the aluminum lake but all, except that of beryllium, are either dissolved or decolorized by ammonium carbonate.

Corey and Rogers[3] have studied the reactions of "Aluminon" with gallium, germanium, indium, scandium and thallium. With the exception of germanium, these elements form red lakes, but they are destroyed by ammonia or ammonium carbonate solutions.

Lundell and Knowles[4] made use of the "Aluminon" reagent in the quantitative determination of small amounts of aluminum in non-ferrous alloys.

Yoe and Hill[5] made an extensive study of the various factors involved in the use of this reagent and developed a method for the colorimetric determination of aluminum in potable water. The method is also applicable to the determination of small quantities of aluminum in salts, minerals, rocks, etc.

In this note we report further studies with "Aluminon." Observations with nineteen elements, most of them rare elements, have been made. In most cases the chloride or nitrate was used; in a few instances the sulfate or oxalate. The concentration of the metallic ion was approximately twenty parts per million in the final dilution, *i. e.*, 0.24 mg. per 12 ml. The "Aluminon" reagent was 0.1% in water solution.

The following procedure was observed. To a measured amount of a given salt the reagents were added in the order listed: (1) 2 ml. of 1 *N* HCl; (2) 2 ml. 3 *N* $NH_4Ac$; (3) 2 ml. "Aluminon," allowed to stand five to

[1] Hammett and Sottery, THIS JOURNAL, **47**, 142 (1925).

[2] Middleton, *ibid.*, **48**, 2125 (1926).

[3] Corey and Rogers, *ibid.*, **49**, 216 (1927).

[4] Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926).

[5] Yoe and Hill, THIS JOURNAL, **49**, 2395 (1927).

ten minutes; (4) 2 ml. 6 *N* $NH_4OH$; (5) 4 ml. 6 *N* $(NH_4)_2CO_3$. The results are recorded in the following table.

TABLE I

ANALYTICAL RESULTS

| Ion | "Aluminon" | $NH_4OH$ | $(NH_4)_2CO_3$ |
|---|---|---|---|
| Arsenic, $As^{+++}$ | Red soln. | Almost decolorizes soln. | Decolorizes soln. |
| Columbium, $Cb^{++}$ | Brownish-red ppt. | Ppt. dissolves giving pale yellow soln. | Decolorizes soln. |
| Dysprosium, $Dy^{+++}$ | Red soln. | Purple soln. | Decolorizes soln. |
| Gadolinium, $Cd^{+++}$ | Red ppt. | Ppt. dissolves giving purple soln. | Decolorizes soln. |
| Hafnium, $Hf^{++++}$ | Deep pink soln. | Light pink soln. | Decolorizes soln. |
| Iridium, $Ir^{++++}$ | Red soln. | Pale yellow soln. | Soln. almost colorless |
| Molybdenum,[a] $Mo^{++++++}$ | Red ppt. | Ppt. dissolves giving pale yellow soln. | Soln. almost colorless |
| Praseodymium, $Pr^{+++}$ | Red ppt. | Ppt. dissolves giving pink soln. | Decolorizes soln. |
| Rhenium[b] | Red soln. | Pale yellow soln. | Soln. almost colorless |
| Rhodium, $Rh^{+++}$ | Brownish-red ppt. | Ppt. dissolves giving pale yellow soln. | Soln. almost colorless |
| Ruthenium, $Ru^{+++}$ | Pink soln. | Pale yellow soln. | Dingy yellow soln. |
| Samarium, $Sm^{+++}$ | Red soln. | Pale purple soln. | Decolorizes soln. |
| Tantalum, $Ta^{+++++}$ | Brownish-red ppt. | Ppt. dissolves giving pale yellow soln | Soln. almost colorless |
| Tellurium,[a] $Te^{++++++}$ | Red soln. | Pale yellow soln. | Scln. almost colorless |
| Thulium, $Tm^{+++}$ | Red soln. | Purple soln. | Decolorizes soln. |
| Tungsten, $W^{++++++}$ | Brownish-red ppt. | Ppt. dissolves giving pale yellow soln. | Soln. almost colorless |
| Uranyl, $(UO_2)^{++}$ | Red soln. | Pale yellow soln. | Soln. almost colorless |
| Vanadium, $V^{++}$ | Scarlet ppt. and soln. | Ppt. partly dissolved, soln. pale pink | Dissolves ppt. |
| Ytterbium, $Y^{+++}$ | Deep pink soln. | Pink soln. | Decolorizes soln. |

[a] The metal was dissolved in *aqua regia*. The ions are assumed to be in the highest state of oxidation.

[b] The metal was treated with *aqua regia* and the mixture evaporated to dryness. Concentrated nitric acid was added to the residue and evaporated to dryness. This treatment was repeated and the residue taken up in distilled water.

An inspection of the table shows that gadolinium, molybdenum, praseodymium and vanadium give red precipitates. All are dissolved and decolorized by ammonia or ammonium carbonate. Columbium, rhodium, tantalum and tungsten give brownish-red precipitates soluble in ammonia and decolorized to a pale yellow. The remaining elements give red or deep pink solutions with "Aluminon," but all were decolorized by ammonia or ammonium carbonate. It is evident that none of the above elements will interfere with the detection of aluminum by the "Aluminon" reagent. Beryllium forms a lake similar to the aluminum lake and hence the reagent does not distinguish between these two elements.

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COBB CHEMICAL LABORATORY
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JOHN H. YOE

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**A Simple Derivation of General Equations of Energy and Entropy of Gases.**—Recently the author,[1] by employing the characteristics of exact differentials, deduced general equations of energy and entropy of gases whose generalized equation of state is

$$p = T\Psi(v) - \Phi(v) - F(v,T) \tag{1}$$

While this method of derivation[2] is exact, it is rather time consuming. The author has now found that these equations can be directly and very easily deduced by using the following two thermodynamic formulas

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \tag{2}$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \tag{3}$$

For, from Equation 1, we have by differentiation at constant volume

$$\frac{\partial p}{\partial T} = \Psi(v) - \frac{\partial F}{\partial T} \tag{4}$$

Substituting Equation 4 into Equation 2 and integrating, we get

$$S = \int \Psi(v)\mathrm{d}v - \int \frac{\partial F}{\partial T}\,\mathrm{d}v + \beta(T) \tag{5}$$

which is the general equation of entropy. Substituting Equations 1 and 4 into Equation 3 and integrating, we get

$$u = \int \Phi(v)\mathrm{d}v + \int \left[F - T\frac{\partial F}{\partial T}\right]\mathrm{d}v + \alpha(T) \tag{6}$$

which is the general equation of energy. The general applicability of Equations 5 and 6 has already been shown.[1]

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[1] Huang, *Phys. Rev.*, **37**, 1171 (1931).

[2] For the detail of derivation by the method of exact differentials see "Science Reports of National Tsinghua University," First Series, Vol. I, No. 3 (in press).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

# THE REACTION OF ALKYL BROMIDES WITH PYRIDINE

BY C. R. NOLLER AND R. DINSMORE

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Although considerable work has been done on the relative ease of replacement of halogen in organic compounds by other groups, the only quantitative work concerning the relative ease of removal of hydrogen halide from organic halides is that of Brussoff,[1] who measured the rate of formation of olefin during the reaction of alkyl halides with alcoholic potassium hydroxide. It is not possible to compare the behavior of the various halides from this work, however, because no attempt was made to determine the rate of side reactions, the extent of which varied from 7 to 83% of the total reaction taking place. A more exact comparison of the rates of removal of halogen acid should be of interest, not only from the standpoint of preparing unsaturated compounds or avoiding their formation, but also as a possible means of determining whether there is any difference in the reactivity or mobility of various types of hydrogen, *i. e.*, primary, secondary or tertiary, comparable to the differences in the reactivity of various types of halogen in replacement reactions. There is also the possibility of correlating these results with the reactivity of the halogen atom and with such reactions as the dehydration of alcohols and the reducing action of the Grignard reagent.

As indicated in a previous note[2] an investigation of the reaction of alkyl halides with tertiary amines was undertaken with the above points in view. The use of tertiary amines for the removal of hydrogen halide from organic halides to form unsaturated compounds is quite well known[3] and has for our purpose an advantage over alkalies in that alcohol would not have to be used as a solvent, and side reactions that would be difficult to follow are avoided. Menschutkin[4] has used triethyl- and triamylamine to follow the rate of formation of quarternary ammonium salts and Clarke and a number of others[5] have used pyridine for the same purpose. Recently Semb and McElvain[3] reported the rate of formation of tertiary amines from piperidine and a large number of organic bromides, and have also reported the relative amounts of tertiary amine and unsaturated hydrocarbon that had been formed at the end of a certain number of hours of reaction. Preliminary investigation of the action of triamylamine, dimethylaniline, pyridine

[1] Brussoff, *Z. physik. Chem.*, **34**, 129 (1900).

[2] Noller and Dinsmore, THIS JOURNAL, **53**, 1185 (1931).

[3] *Cf.* Semb and McElvain, *ibid.*, **53**, 690 (1931), Ref. 2.

[4] Menschutkin, *Z. physik. Chem.*, **5**, 589 (1890); **6**, 41 (1890).

[5] Clarke, *J. Chem. Soc.*, **97**, 416 (1910); **99**, 1927 (1911); **101**, 1788 (1912); **103**, 1689 (1913); Norris, THIS JOURNAL, **50**, 3042 (1928); Kerr, *J. Chem. Soc.*, 239 (1929); Mukhin, *Chem. Abstracts*, **24**, 2942 (1930); Tronov, *ibid.*, **24**, 590 (1930).

and quinoline, indicated that pyridine was most satisfactory for our purpose.[6] By titrating the reaction mixture first with standard alkali and then determining the amount of ionized halogen in the same solution by the Volhard method, we have been able to follow the rates of formation of both hydrogen ion and total bromide ion. The difference between the two gives the rate of formation of pyridinium bromide, a reaction that appears to take place independently but simultaneously with the removal of hydrogen bromide. While the incidence of side reactions prevents exact comparisons, it is believed that the results obtained express at least semi-quantitatively the relative ease of removal of hydrogen halide, that they give values for the rates of formation of pyridinium halides in agreement with previous work on the reactivity of the halogen atom in organic compounds, and that they throw considerable light on the mechanism of the reaction as a whole.

## Experimental Part

**Reagents. Pyridine.**—A commercial refined pyridine was dried over solid potassium hydroxide and carefully fractionated through a 1-meter column of the Vigreux type. After the vapors reached the boiling point of pyridine, a large forerun was removed and a middle cut boiling at 114.8–115.2° was used.

**Alkyl Bromides.**—The ethyl bromide was a commercial product, *t*-butyl bromide was prepared from the alcohol and acetyl bromide, and the remaining bromides were prepared from the alcohol and phosphorus tribromide at 0°. All bromides were thoroughly washed with cold concentrated sulfuric acid, allowed to stand over anhydrous potassium carbonate with occasional shaking until sweet and free from acid, and fractionally distilled. The boiling point ranges were as follows: ethyl, 38.8–39.3°; *n*-propyl, 70.7–70.9°; *i*-propyl, 60.4–61.1°; *n*-butyl, 100.8–101.4°; *i*-butyl,[7] 91.3–92.9°; *s*-butyl, 91.8–92.8°; *t*-butyl, 71–73°.

**General Procedure.**—Bulbs of about 10 cc. capacity were blown from 13-mm. Pyrex tubing, drawn out and sealed to 5 mm. tubing. Pyridine and alkyl bromide were weighed directly into a glass-stoppered flask (mol. ratio 1:11) and well mixed. From this mixture, 5 cc. portions were pipetted into the tared bulbs, the bulbs sealed and

[6] There is the possibility of an exchange of organic radicals if the alkyl amines are used, while quinoline gives colored products with the alkyl bromides. Thus *n*-butyl bromide gave a deep red solution when heated with quinoline and a red resinous solid was isolated from the reaction mixture. The nature of this product was not investigated.

[7] This material was found to contain from 0.8 to 1.2% *t*-butyl bromide when analyzed according to the method of Michael, *Ann.*, **379**, 287 (1911), and was used for some of the preliminary work. Subsequent results were obtained with material that boiled at 91.6–91.8° and which contained less than 0.1% of *t*-butyl bromide. This was prepared by heating eleven moles of bromide with one mole of pyridine in sealed bulbs for three hours at 148.8°, after which the bulbs were cooled and opened, the bromide decanted, washed four times with cold concentrated sulfuric acid, shaken with anhydrous potassium carbonate until free of acid and fractionated. Subsequent work indicated that simply refluxing for three hours with the pyridine should be sufficient. This treatment for the removal of tertiary bromide is much more economical than the hydrolytic procedure of Michael.

weighed again. The bulbs were fitted to corks which fit into holes in the cover of the constant temperature (148.8 ± 0.2°) bath. The holes in the cover were large enough to permit the passage of the bulb so that bulbs could be withdrawn without removing the cover. The bulbs were withdrawn at intervals and plunged at once into an ice-water-bath. The small part of the bulb was opened, connected to a water pump and the excess bromide completely distilled at room temperature.[8] The bulb was then broken in a heavy-walled beaker, the contents dissolved in water and titrated with 0.1 *N* standard sodium hydroxide solution to a distinct pink color with phenolphthalein. Care was taken not to overstep the end-point. The same solution was then acidified with dilute nitric acid and the total bromide ion determined by the Volhard method.[9] The rate of reaction of *t*-butyl bromide was too rapid to measure at 148.8° and it was run at 92.0°, together with *s*-butyl bromide at the same temperature for comparison.

## Discussion of Results

Before attempting to analyze the experimental data, a few remarks should be made concerning the procedure used. The temperature chosen was that at which most of the rates could be determined within a reasonable time. A large excess of one of the reagents was used in order to increase the rate of reaction, and so that the reaction might be considered as pseudo-monomolecular. The choice of the bromide for the excess reagent seems, in the light of the results obtained, to have been unfortunate. In the first place the alkyl pyridinium bromides and pyridine hydrobromides are insoluble in the alkyl bromide and precipitate during the course of the reaction. In the second place the excess bromide appears to be the cause of an apparent reaction greater than 100%. This point will be discussed later.

When the amounts of hydrogen ion and of total bromide ion were plotted against the time, typical curves for monomolecular reactions were obtained. It was found that the amount of hydrogen bromide approached an approximately constant value which was less than that approached by the total bromide ion; that is, barring the unlikely assumption that the quaternary ammonium salt is in equilibrium with pyridine hydrobromide and unsaturated hydrocarbon,[10] two independent reactions are taking place, the direct removal of hydrogen bromide and the formation of alkyl-pyridinium bromide. Therefore the formation of quaternary ammonium salt is not an intermediate step in the removal of hydrogen bromide.

[8] In the early runs the excess bromide was not removed and in some cases interfered with the titrations.

[9] Blanks were run in all cases to determine the extent of the reaction taking place before immersion in the bath, and at least two runs made on each bromide. Results could be readily duplicated to within less than 2%.

[10] Direct evidence against this assumption is the fact that *t*-butyl bromide is completely converted into pyridine hydrobromide whereas *i*-butyl bromide gives a mixture of pyridine hydrobromide and *i*-butylpyridinium bromide. Since both bromides yield the same olefin, any equilibrium would necessitate the final reaction mixture having the same composition in both cases.

Accordingly the values for the amount of pyridine hydrobromide were subtracted from the corresponding values for the total bromide ion in order to obtain the amount of alkylpyridinium bromide formed. If now the two independent reactions are both pseudomonomolecular, the ratio of pyridine hydrobromide to alkylpyridinium bromide should be constant. This was

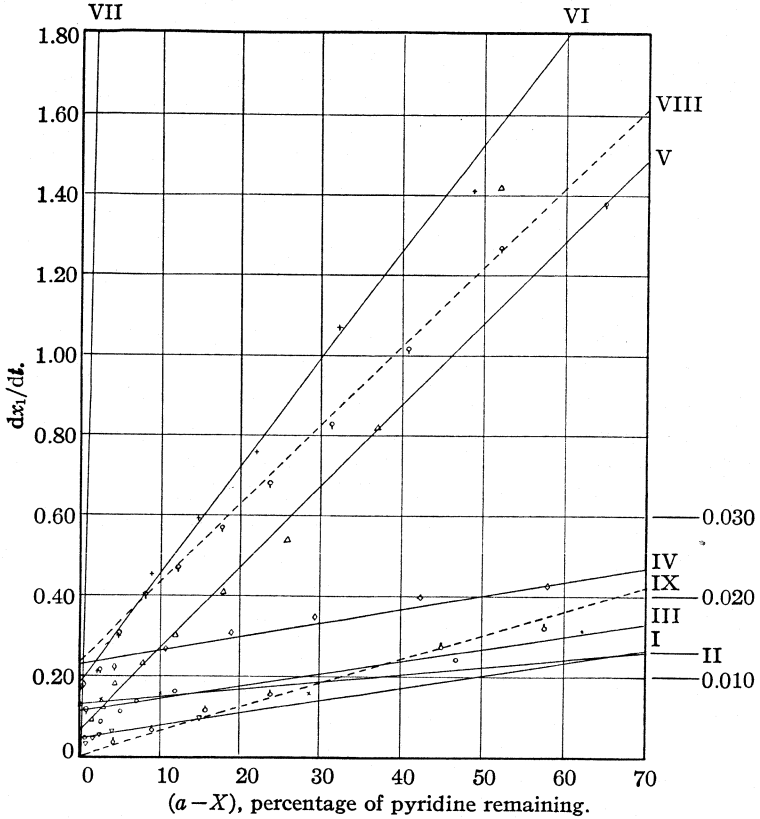


Fig. 1.—Change in rate of formation of pyridine hydrobromide, solid curves at 148.8°; I, ethyl, ▽; II, *n*-butyl, ×; III, *n*-propyl, ○; IV, isobutyl, ◇; V, isopropyl, △; VI, *sec.*-butyl, +; VII, *tert.*-butyl, calculated from measurements at 92°. Dotted curves at 92°: VIII, *tert.*-butyl, ○; IX, *sec.*-butyl, ○, scale at right.

found to be approximately so especially for the earlier part of the reaction but not sufficiently constant to give the data a purely analytical treatment. We therefore plotted the data and graphically determined the change in the rates of formation at different times. These values were then plotted against the percentage of pyridine remaining, as shown in Figs. 1 and 2. Using the formula $dx/dt = K(a-X)$ where $X$ is the total bromide ion formed, that is, $x_1 + x_2$, it follows that the slopes of these curves corre-

spond to the velocity constants $K$ which have been summarized in Table I. The relative rates of reaction taking the rate for *n*-butyl bromide as unity have also been included in the table.

At 148.8° the rate of reaction of *t*-butyl bromide was so great that not even an approximate velocity constant could be determined. To obtain such an approximation, the rate was measured at 92° together with that of

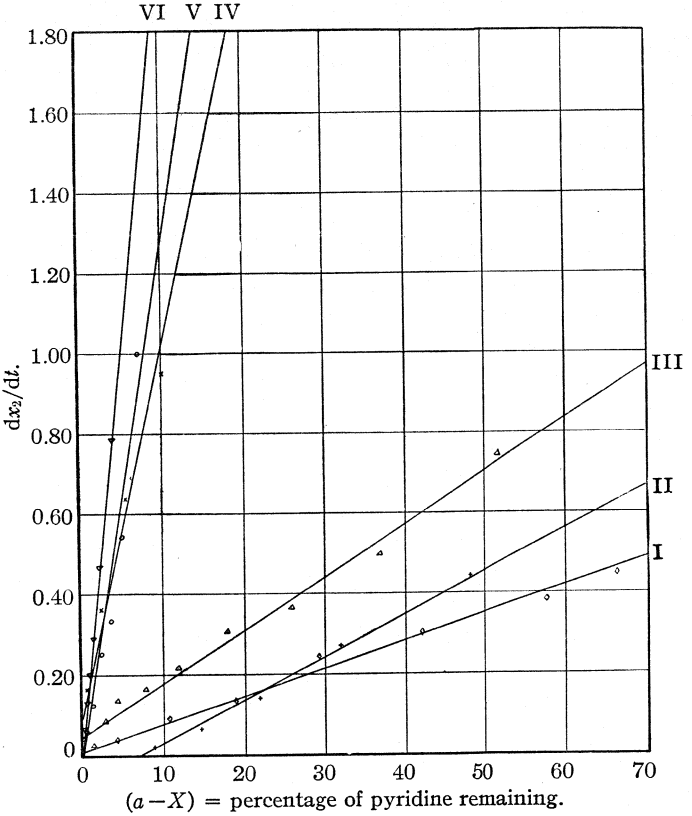


Fig. 2.—Change in rate of formation of alkylpyridinium bromide at 148.8°: I, isobutyl, ◇; II, *sec.*-butyl, +; III, isopropyl, △; IV, *n*-butyl, ×; V, *n*-propyl, ⊙; VI, ethyl, ▽; *tert.*-butyl not measurable—slope probably less than isobutyl.

*s*-butyl bromide at the same temperature. It was found that *t*-butyl bromide gave entirely pyridine hydrobromide and no quaternary salt within the limits of experimental error. The rate of formation of pyridine hydrobromide from *s*-butyl bromide at 92° was 1/89 of that at 148.8°, and therefore the rate of formation of pyridine hydrobromide from *t*-butyl bromide at 148.8° was estimated as 89 times that at 92°.

It is apparent that, from a practical standpoint, the method of removing

TABLE I

VELOCITY CONSTANTS AND RELATIVE RATES OF FORMATION OF PYRIDINE HYDROBROMIDE AND OF ALKYLPYRIDINIUM BROMIDE FROM VARIOUS ALKYL BROMIDES AT 148.8°

| Alkyl bromide | Pyridine hydrobromide $K_1$ | Pyridine hydrobromide Rel. rate of formation | Alkylpyridinium bromide $K_2$ | Alkylpyridinium bromide Rel. rate of formation | Conant's "Relative reactivity of alkyl chlorides" |
|---|---|---|---|---|---|
| Ethyl | 0.003 | 1.5 | 0.200 | 2.1 | 1.9–2.5 |
| *n*-Propyl | .003 | 1.5 | .129 | 1.4 | 1.0–1.1 |
| *i*-Propyl | .020 | 10.0 | .013 | 0.14 | 0.015 |
| *n*-Butyl | .002 | 1.0 | .094 | 1.0 | 1.0 |
| *i*-Butyl | .003 | 1.5 | .007 | 0.07 | ... |
| *s*-Butyl | .027 | 13.5 | .008 | .09 | 0.022 |
| *t*-Butyl (calcd.) | 1.75 | 875.0 | ... | .. | .018 |
| *s*-Butyl (at 92°) | 0.0003 | | | | |
| *t*-Butyl (at 92°) | .0197 | | | | |

hydrogen halide from organic compounds by means of tertiary amines would not be applicable to primary halides and would be only moderately successful for secondary halides, with the possible exception of alicyclic compounds such as cyclohexyl bromide, which appears to lose hydrogen bromide quite readily.[3] For tertiary halides the method should be quite satisfactory.

**Comparison with Results of Other Investigators.**—Comparing the relative rates of formation of alkylpyridinium bromide, taking the velocity coefficient of *n*-butyl chloride as unity, with the relative "reactivities" of the chlorine atom as determined by Conant and Hussey,[11] we find substantially qualitative agreement. That is, the primary halides are more reactive than the secondary. While Conant's results indicate a 100-fold difference and ours only a 10-fold difference, this might readily be accounted for by the fact that the comparison is between chlorides on the one hand and bromides on the other. As has been often noted, the ethyl compound is considerably more reactive than the higher normal halides. Unfortunately we have not been able to make accurate measurements for quaternary salt formation on *t*-butyl bromide, and Conant gives no data on *i*-butyl chloride. Our results seem to indicate that although *i*-butyl bromide is a primary halide its rate of reaction is of the same order as the secondary halides. Conant has found that the branching of the carbon chain in the case of *i*-amyl chloride causes the relative reactivity to drop from 1.26 to 0.65 and from our results it appears that when the side chain is closer to the halogen atom the rate is still more markedly decreased. This is also in agreement with the work of Semb and McElvain, who found that after forty-eight hours the percentage reaction with piperidine was *n*-amyl, 90.5, isoamyl, 77.4 and isobutyl, 40.8.

Considering what is probably the more important part of this work,

[11] Conant and Hussey, THIS JOURNAL, **47**, 476 (1925).

because no other satisfactory quantitative work has been done along this line, namely, the relative ease of removal of hydrogen halide, we find that the order of relative rates of formation of pyridine hydrobromide is the reverse of that of the relative rates of formation of alkylpyridinium bromide; that is, the primary halides lose hydrogen bromide least readily and the rates for all of them are of the same order. The secondary halides lose hydrogen bromide seven to nine times as fast as the fastest reacting primary halide, while the only tertiary bromide studied loses hydrogen bromide about 80 times more rapidly than the secondary halides and about 800 times more rapidly than the primary halides.[12] In fact, in the case of *t*-butyl bromide hydrogen bromide is lost so readily that the rate of quaternary salt formation could not be determined.

This order is the same as that found for such reactions as the hydrolysis of alkyl bromides in neutral solution[13] and the dehydration of alcohols.[14]

It has also been pointed out[15] that only tertiary halides give satisfactory yields of hydrocarbons with zinc alkyls.[16]

[12] Because of the side reactions taking place, some of the values for the individual rate constants may be in error by as much as 100%. This, however, does not alter the general conclusions in regard to the relative reactivity of the different types of halides, as can be readily seen from Figs. 1 and 2.

[13] Nicolet and Stevens, THIS JOURNAL, **50,** 135 (1928); Straus, *Ann.*, **370,** 366 (1909); Michael, Ref. 7.

[14] Adkins and Perkins, THIS JOURNAL, **47,** 1163 (1925); Adkins and Lazier, *ibid.*, **47,** 1719 (1925); **48,** 1671 (1926).

[15] Noller, *ibid.*, **51,** 597 (1929).

[16] It is of interest to note that in those reactions where the order of reactivity is primary > secondary, namely, the reactions with inorganic iodides, thiosulfates, alkali alcoholates, enolates and phenolates, one reactant is an ion, whereas in those reactions where the order is tertiary > secondary > primary only non-polar molecules are involved. In view of the recent work of Herzfeld and Scheibe, *Z. physik. Chem.*, **7B,** 390 (1930), which shows that the photochemical dissociation of methyl halides is into radicals and halogen atoms, it seems entirely possible that those reactions where the first order holds involve the removal of the halogen as an ion, whereas in those reactions where the second order holds, the halogen leaves the molecule as an atom. It is readily conceivable that both types of reaction may take place with pyridine if one assumes that when hydrogen bromide is removed, the hydrogen and bromine are removed simultaneously as atoms and that when quaternary salt formation takes place, the halogen separates as ion.

An alternative hypothesis is that the order of the true relative lability of the halogen is tertiary > secondary > primary and that in the reaction of large groups such as the ionic reactants and amines, "steric hindrance" plays an overwhelming role. This is partly supported by the behavior of *n*-amyl and *i*-amyl, and *n*-butyl, and *i*-butyl compounds. "Steric hindrance" would not be likely to play a large part in the case of small molecules such as water and alcohol, nor in reactions such as the dehydration of alcohols or the elimination of hydrogen bromide. On the other hand, one is at a loss to explain on this basis why large molecules such as zinc di-*n*-butyl react only with tertiary halides and why the hydrolysis of esters is so markedly affected by "steric hindrance." Moreover, if "steric hindrance" determines the course of the reaction

**Side Reactions.**—The most obvious inaccuracy of our experimental method is the fact that the total amount of reaction goes to a greater or less degree above 100%, the maximum being 108%. We have been unable to detect impurities such as phosphates, sulfates, silicon or boron compounds after typical runs when the reaction has been allowed to proceed above 100%, and the same results are obtained in quartz as in Pyrex tubes. The plotted data show that beyond the point where all the pyridine has reacted, the increase in hydrogen ion is approximately equal to the increase in total reaction. That is, the formation of quaternary ammonium salt stops as soon as all the pyridine is gone but the formation of titratable hydrogen ion continues. Moreover, the formation of this excess hydrogen bromide reaches equilibrium with some other product of the reaction, probably unsaturated hydrocarbon. The following series of experiments illustrate these points.

Six Pyrex tubes and one fused silica tube containing pyridine and excess isopropyl bromide (molar ratio 1:11) were heated at 148.8° for two and one-half hours, the time previously shown to be sufficient to reach complete reaction. All tubes were removed and cooled, and two Pyrex tubes and the quartz tube set aside for analysis. The remaining four Pyrex tubes were distilled to dryness at room temperature *in vacuo*. Two of these were

TABLE II

EXPERIMENTS ON SIDE REACTIONS

| | $H^+$, % | Total $Br^-$ | Alkylpyridinium bromide |
|---|---|---|---|
| Pyrex tubes heated two and one-half hours | 72.7 | 101.9 | 29.2 |
| | 73.0 | 101.5 | 28.5 |
| Fused silica tube heated two and one-half hours | 72.7 | 101.3 | 28.6 |
| Tubes from which excess bromide was distilled after two and one-half hours and which were resealed and heated for an additional two and one-half hours | 72.9 | 100.7 | 27.8 |
| | 72.6 | 101.3 | 28.7 |
| Tubes treated as above except that fresh bromide was added before resealing | 79.3 | 108.1 | 28.8 |
| | 80.6 | 108.1 | 27.5 |

one might expect the total rate in the reaction with pyridine to be markedly decreased with the primary halides whereas one actually finds that the total rate of reaction of the primary halides is greater than that of the secondary halides.

One of the Referees has suggested that the mechanism of the removal of hydrogen halide may consist of the incipient withdrawal of a hydrogen ion, because of the capacity of a tertiary amine to accept a proton, which would promote the liberation of halogen as anion; and that tertiary halides lose hydrogen halide more readily than secondary or primary because of the greater number of hydrogen atoms available for elimination of hydrogen halide. Such an explanation would apply also to the dehydration of the alcohols but not to the hydrolysis of the alkyl halides. Of course, there is no reason for supposing that all three reactions have a common mechanism other than the fact that they show the same order of reactivity for the different types of compounds.

then resealed and to each of the remaining two tubes was added eleven moles more of pure *i*-propyl bromide. These were then sealed and all four tubes heated at 148.8° for another two and one-half hours. The results are given in Table II.

The only way in which we have been able to account for these results is to assume that the excess bromide decomposes under the action of heat to give hydrogen bromide, which combines in some unknown way with the other products of the reaction to give a product which is sufficiently stable to prevent loss of hydrogen bromide during the distillation of the excess bromide and yet sufficiently unstable to be in equilibrium with the unsaturated hydrocarbon at the temperature of the reaction.

The fact that the amount of quaternary ammonium salt does not change on prolonged heating indicates that the Ladenburg rearrangement of alkylpyridinium halides to alkyl pyridine hydrohalides takes place to only a very slight extent under the conditions of our experiments and in most cases there is no indication that it takes place at all. What might be interpreted as Ladenburg rearrangement is most marked in the case of *n*-butyl bromide, where the amount of quaternary ammonium salt decreased to the extent of about 2% four hours after it had reached its maximum value.

Still another side reaction seems to take place in the case of *i*-butyl bromide. The experimental data show that the curve for the rate of formation of pyridine hydrobromide actually crosses that for quaternary salt formation. We believe that this anomalous behavior is due to the rearrangement of *i*-butyl bromide to *t*-butyl bromide, which then reacts very rapidly with the pyridine to form almost exclusively pyridine hydrobromide.

## Summary

1. The total rates of reaction with pyridine, and the rates of formation of pyridine hydrobromide have been determined for the seven alkyl bromides from ethyl to butyl. The results indicate that the removal of hydrogen bromide and quaternary salt formation are two simultaneous independent reactions.

2. The order for the relative rates of quaternary salt formation is primary > secondary, which is in accordance with the results of previous investigators on metathetical reactions where the second reactant is an ion.

3. The order for the relative rates of removal of hydrogen bromide is tertiary > secondary > primary, which is the same as that known to exist for the relative rates of hydrolysis and alcoholysis of alkyl halides, and for the relative rates of dehydration of alcohols.

4. The method of removing hydrogen halide from organic compounds by means of tertiary amines appears to be applicable to tertiary halides and less successfully to secondary halides but inapplicable to primary halides.

5. Under the present experimental conditions, the Ladenburg rearrangement does not take place to an appreciable extent. A rather unsatisfactory explanation is given for the fact that the total reaction appears to proceed to an extent greater than 100%. Rearrangement of *i*-butyl to *t*-butyl bromide appears to take place during the course of the reaction and this probably accounts for the anomalous behavior of *i*-butyl bromide.

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[CONTRIBUTION NO. 15 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

# REDUCTION OF NITROGUANIDINE. I. PRELIMINARY STUDY OF THE OXIDATION POTENTIAL OF THE NITRO-NITROSOGUANIDINE SYSTEM[1]

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## Introduction

Nitroguanidine as an oxidizing agent has been only superficially studied and it is of peculiar interest because of the variety of reduction products which may be obtained from this substance and because of its close analogy to such important substances as nitric acid and nitrobenzene on the one hand and hydrazine and aniline on the other. Since it was thought that a knowledge of the free energy changes and the equilibrium constants for the reactions involved in the reduction of nitroguanidine would be of aid in furthering the studies on this topic, it was decided to attempt to measure the e. m. f. developed by the various nitroguanidine or derived systems.

The first system chosen for study was nitro–nitrosoguanidine, because nitrosoguanidine was the first definite reduction product of nitroguanidine known at that time and also because the preparation and properties of nitrosoguanidine were being studied in this Laboratory.

**Theoretical Considerations.**—It has been known from the work of Thiele in 1893[2] that nitroguanidine may be reduced to nitrosoguanidine in acid solution by nascent hydrogen (*i. e.*, zinc). If we assume that the reaction proceeds in accordance with the equation

$$C(=NH)(NH_2)(NHNO_2) + 2H^+ + 2\ominus \longrightarrow C(=NH)(NH_2)(NHNO) + H_2O \qquad (I)$$

[1] This paper was constructed from part of the thesis submitted by Mr. Sabetta to the faculty of the Polytechnic Institute of Brooklyn in June, 1931, in partial fulfilment of the requirements for the degree of Master of Science in Chemistry. It was presented before the Division of Physical and Inorganic Chemistry at the Eighty-second meeting of the American Chemical Society in Buffalo, N. Y., August 31 to September 4, 1931.

[2] Thiele, *Ann.*, **273**, 133 (1893).

the e. m. f. developed by the change from the higher state of oxidation (nitroguanidine-$RNO_2$) to the lower state (nitrosoguanidine-RNO) may be calculated from the familiar Peter's equation, provided the reaction is reversible

$$E_{Obs.} = E_0 - 0.03 \log \frac{(c_{RNO})}{(c_{RNO_2})(c_{H^+})^2} \qquad (II)$$

where $[c_{H^+}]$ has the customary meaning and $(c_{RNO})$ and $(c_{RNO_2})$ are the effective concentrations of nitrosoguanidine and nitroguanidine, respectively. If the normal oxidation potential, $E_0$, is a constant when calculated by the above equation from the observed e. m. f., $E_{Obs.}$, developed by various concentrations of the reactants, the reduction of nitroguanidine to nitrosoguanidine is a reversible reaction and obeys the general law of inorganic oxidation systems.

## Experimental Part

**Apparatus.**—The apparatus used in making these measurements of e. m. f. consisted of a Leeds and Northrup "Hydrogen Ion Potentiometer" (No. 7665), a Leeds and Northrup galvanometer with lamp and scale (No. 2420-0) and the usual accessories.

**Materials: Nitroguanidine.**—Pure nitroguanidine, prepared by the method described by Smith, Sabetta and Steinbach,[3] was weighed and dissolved in recently boiled distilled water and diluted to the desired volume. The solutions were prepared each day because of the slow hydrolysis of nitroguanidine in water even at room temperature.

**Nitrosoguanidine.**—Nitrosoguanidine was prepared by reducing nitroguanidine with zinc powder in a solution of ammonium chloride.[4] Solutions were prepared by the vigorous agitation for five minutes at room temperature of a large excess of nitrosoguanidine in contact with previously boiled distilled water. The solutions were filtered, analyzed by titration with a solution of permanganate and used immediately.

**Standard Buffer Solutions.**—Buffer solutions were prepared as recommended by Clark[5] except that they were of twice the concentrations given by Clark. The solutions were checked by diluting with equal volumes of water and measuring e. m. f. with the usual hydrogen electrode.

**Electrodes.**—Initially, polished platinum foil, platinized platinum foil, platinum wire and silver wire were used as the inert contact electrode. Finally, either polished or platinized platinum foil (1 sq. cm. in area) was adopted. As is quite generally the case in this type of measurement, detailed attention had to be given to the cleanliness of the electrodes. What is essentially Popoff's[6] method was used in preparing the electrodes; after thorough washing with a concentrated solution of potassium hydroxide, they were electrolyzed as anode in a concentrated solution of hydrochloric acid and then plated in the Popoff platinum solution; subsequently they were washed with distilled water, electrolyzed in a 3 *M* solution of sodium hydroxide and then in a 3 *M* solution of sulfuric acid. They were rinsed with distilled water and preserved in distilled water

[3] Smith, Sabetta and Steinbach, *Ind. Eng. Chem.*, **23**, 1124 (1931).

[4] The details of the preparation and properties of nitrosoguanidine and the analytical methods for its determination, the experimental work upon which is complete, will constitute the subject matter of the third paper of this series.

[5] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 1929, pp. 200–201.

[6] Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

(protected from the air) until used. The polished platinum electrodes were treated in the same manner with the exception that they were not electrolyzed in the platinum solution.

**Method.**—In this study, mixtures of pure nitroguanidine and nitrosoguanidine were taken. Measured volumes of standard solutions of nitroguanidine and nitrosoguanidine were taken, and to this mixture was added 50 cc. of the desired buffer solution and the entire solution diluted to 100 cc. Two electrode vessels were used for the nitro–nitrosoguanidine system; in one a polished platinum electrode was in contact with the solution and in the other a platinized platinum electrode. The e. m. f. of

TABLE I

MEASUREMENTS OF THE E. M. F. OF THE NITRO–NITROSOGUANIDINE OXIDATION SYSTEM

| Concentration of nitroguanidine $\times 10^{-4}$ | Concentration of nitrosoguanidine $\times 10^{-4}$ | $P_H$ | Observed e. m. f., volt | Calcd. normal electrode potential referred to H electrode as 0 |
|---|---|---|---|---|
| 15.44 | 10.00 | 3 | 0.462 | 0.885 |
| 30.88 | 10.00 | 3 | .468 | .879 |
| 46.32 | 14.50 | 3 | .471 | .882 |
| 15.44 | 12.76 | 3 | .460 | .883 |
| 20.00 | 20.00 | 3 | .456 | .882 |
| | | | | Av. .882 |
| 27.70 | 6.38 | 5 | .354 | .881 |
| 55.40 | 6.38 | 5 | .360 | .878 |
| 83.10 | 6.38 | 5 | .365 | .878 |
| 27.70 | 12.76 | 5 | .350 | .886 |
| 27.70 | 25.52 | 5 | .336 | .881 |
| 20.00 | 20.00 | 5 | .335 | .881 |
| | | | | Av. .881 |
| 27.70 | 2.52 | 6 | .311 | .886 |
| 55.40 | 2.52 | 6 | .316 | .882 |
| 83.10 | 2.52 | 6 | .321 | .881 |
| 111.00 | 2.52 | 6 | .326 | .883 |
| 27.70 | 5.04 | 6 | .302 | .885 |
| 27.70 | 10.09 | 6 | .292 | .885 |
| 20.00 | 20.00 | 6 | .277 | .883 |
| | | | | Av. .883 |
| 27.70 | 8.88 | 7 | .209 | .860 |
| 27.70 | 26.64 | 7 | .207 | .873 |
| 83.10 | 4.44 | 7 | .223 | .851 |
| 20.00 | 20.00 | 7 | .202 | .868 |
| | | | | Av. .863 |
| 27.70 | 4.44 | 8 | .145 | .847 |
| 27.70 | 8.88 | 8 | .136 | .847 |
| 83.10 | 4.44 | 8 | .160 | .848 |
| 20.00 | 20.00 | 8 | .125 | .851 |
| | | | | Av. .848 |

the nitro–nitrosoguanidine half-cell was determined by measuring the e. m. f. of the cell

$$\mathrm{Hg} \left| \mathrm{Hg_2Cl_2\,(satd.\,KCl)} \right\| \mathrm{KCl\,(satd.)} \left\| \begin{matrix} \mathrm{RNO_2} \\ \mathrm{RNO} \\ \mathrm{H^+} \end{matrix} \right| \mathrm{Pt}$$

The e. m. f. of each cell (platinized electrode and polished electrode) was taken alternately every two minutes until both gave the same constant reading to plus or minus 5 millivolts (generally 1 mv.). This was usually accomplished within fifteen minutes, and equilibrium was attained by continuous tapping on the heavy copper leads to secure agitation of the solutions. The results are tabulated in Table I.

## Discussion of Results

Preliminary measurements of e. m. f. developed by the nitro–nitrosoguanidine electrode in solutions where the $[c_{H^+}]$ were obtained by addition of a standard solution of hydrochloric acid gave results which followed the Peter's equation approximately and showed quite conclusively that the system under study was reversible. When $[c_{H^+}]$ was accurately controlled by means of buffered solutions, the agreement from $P_H$ 3, 5 and 6 was very satisfactory, giving a maximum deviation from the mean of 4 mv. and an average of 2 mv. At $P_H$ 8, however, the mean value is 34 mv. less than in the acid range, while at $P_H$ 7 the individual measurements seem to oscillate between the two extreme values, but the concordance of observations is better at $P_H$ 8 than in the acid range. Moreover, equilibrium is attained more quickly at $P_H$ 8, and here and at $P_H$ 7 a silver wire electrode gave readings checking with the carefully prepared platinum electrodes to 1 mv. These apparent discrepancies are probably not due to inaccuracies of the buffer solution at $P_H$ 8.

In connection with these discrepancies, it is interesting to recall certain facts concerning the chemistry of nitrosoguanidine. This substance is readily soluble in either acidic or alkaline solution but only sparingly soluble in water. In alkaline solution it forms insoluble salts with metallic ions such as $Ag^+$, $Cu^{++}$ and $Ni^{++}$[2], and in acid solutions salts are also formed; *e. g.*, the hydrochloride salt is known.[2] These facts indicate that nitrosoguanidine is an amphoteric substance and that an intramolecular rearrangement takes place as follows

$$\mathrm{C}\begin{matrix} \diagup \mathrm{NH_2} \\ = \mathrm{NH} \\ \diagdown \mathrm{NHNO} \end{matrix} \underset{\text{acid}}{\overset{\text{Alkaline}}{\rightleftharpoons}} \mathrm{C}\begin{matrix} \diagup \mathrm{NH_2} \\ = \mathrm{NH} \\ \diagdown \mathrm{N{=}N{-}OH} \end{matrix} \qquad \text{(III)}$$

Both formulas have been suggested by Thiele.[2] Such changes of oxidation potential with $P_H$ are quite common in organic systems,[7] and are attributed by Clark and other workers to changes in ionization of the reductant, which cause less or more $[H^+]$ to be consumed in the

[7] Clark, *Chem. Rev.*, **2**, 127 (1926).

reaction. This treatment leads to the conclusion that three moles of $[H^+]$ are consumed in the reduction of nitroguanidine in alkaline solution. The authors are not prepared at present to postulate a mechanism for the reaction on that assumption.

The reduction of nitroguanidine to nitrosoguanidine is a reversible reaction and proceeds in accordance with equation (I) in acid solution and according to some other mechanism in alkaline solution.

The value of the normal oxidation potential of the nitro–nitrosoguanidine system, 0.88 volt, places it between the mercuric–mercurous system, 0.92 volt, and the ferric–ferro system, 0.71 volt. This is also in agreement with other observations made in this Laboratory concerning the chemistry of nitrosoguanidine.[8] It is worthy of note that these equilibrium potential measurements were made by using pure mixtures of the reactants.

Since the normal oxidation potential is referred to the hydrogen electrode as 0, $E_0$ (0.882 volt in acid solution) is a measure of the work necessary to transform one mole of nitroguanidine to nitrosoguanidine by one mole of hydrogen.[9] Hence $(-\Delta F) = NFE = 40.7$ Kg. Cal. in acid solution. It follows logically, therefore, that the free energy of the reaction taking place in passing from acid to alkaline solution $(-\Delta F)$, is at least 1.6 Kg. Cal. This may be the free energy of ionization.

If the equation for the observed electromotive force of the nitro–nitrosoguanidine system is written in the form

$$E_{\text{Obs.}} = 0.03 \log \frac{(c_{\text{RNO}_2})\,(c_{\text{H}})^2 K}{(c_{\text{RNO}})} \qquad \text{(IV)}$$

then

$$K = \frac{(c_{\text{RNO}})}{(c_{\text{RNO}})\,(c_{\text{H}})^2} \qquad \text{(V)}$$

at equilibrium, and when the effective hydrogen-ion concentration is one, the equilibrium constant $10^{-29.4}$ is the ratio of concentrations of nitrosoguanidine to nitroguanidine in molar acid solution existing at equilibrium with a normal hydrogen electrode. This equilibrium ratio may be computed for other hydrogen-ion concentrations, since

$$K(c_{\text{H}})^2 = \frac{(c_{\text{RNO}})}{(c_{\text{RNO}_2})} \qquad \text{(VI)}$$

and it is seen that this ratio drops rapidly in the alkaline range. Therefore at $P_{\text{H}}$ 14 the ratio would be $10^{1.4}$. This is in accord with the observation made in this Laboratory several years ago that it was not possible to reduce nitroguanidine with zinc and concentrated sodium hydroxide.[10]

[8] The effect of various reducing agents upon nitroguanidine will constitute the subject matter of the second paper of this series to be published in the near future. See also Ref. 2.

[9] In connection with these deductions the authors are pleased to acknowledge their indebtedness to the paper by La Mer and Baker, THIS JOURNAL, **44**, 1954 (1922).

[10] Steinbach, Thesis for M. S. in Chemistry, Polytechnic Institute of Brooklyn, 1927.

If we could maintain constancy of ratio between nitroguanidine and nitrosoguanidine, (II) could be simplified to

$$E_{Obs.} = E_0 - K'' - 0.06 \log P_H$$

and

$$P_H = \frac{K' - E_{Obs.}}{0.06}$$

and we should have a simple and convenient means of determining hydrogen-ion concentrations. An intermediate reduction product between nitroguanidine and nitrosoguanidine having the composition $2RNO \cdot 3RNO_2$ has been isolated and identified as a compound by analysis and properties.[11] A solution of this substance at $P_H$ 7 gave the following measurements: $E_{Obs.}$, 0.206 (with polished and platinized platinum electrodes) and 0.215 (with silver wire); $E_0$ calcd., 0.867 volt and 0.876 volt. Moreover, it has been found possible to titrate sodium hydroxide against hydrochloric acid with this electrode.[12]

Since the normal oxidation potential, 0.88 volt, of this system is higher than that of the quinhydrone system, and higher than some values given for the hydroxyl–oxygen system, it is possible that the nitro–nitrosoguanidine electrode will not be subject to the disadvantages of the hydroquinone electrode in the alkaline region.

The authors are pleased to acknowledge their indebtedness to Professor B. P. Caldwell for his many valuable suggestions during the progress of this work.

## Summary

1. The reduction of nitroguanidine to nitrosoguanidine is a reversible reaction.

2. The normal oxidation potential of the nitro–nitrosoguanidine system is 0.88 volt (free energy 40.7 Kg. Cal.) in acid solution.

3. Calculation from the equilibrium constant shows that it is not feasible to reduce nitroguanidine in strongly alkaline solution with hydrogen.

4. It is suggested that the nitro–nitrosoguanidine electrode may prove useful as a $P_H$ indicator for the alkaline region.

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[11] This substance will be described in a subsequent communication.

[12] Further work is projected in this Laboratory to develop this electrode as a practical indicator of $P_H$ measurements.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

# THE REACTIVITY OF THE METHYLATED SUGARS. VI. THE ACTION OF DILUTE ALKALI ON 3-METHYLGLUCOSE[1]

BY DONALD J. LODER WITH W. LEE LEWIS

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It has been previously shown[2] that when tetramethylglucose is treated with lime water, tetramethylmannose is formed but no methylated ketose. Moreover, the reaction mixture shows a higher iodine absorption than can be accounted for by the presence of the aldoses. When the reaction mixture is treated with acid, the iodine absorption drops to a value corresponding to 100% aldose. These results were explained by postulating that because of the methyl group on the second carbon atom in tetramethylglucose, only the 1,2-enediol can form, in this case a monomethyl-enediol, thus limiting the alkali conversion to the epimeric tetramethylmannose and precluding the formation of ketose. The high iodine absorption value of the neutral or alkaline reaction mixture is believed to be due to the presence of an enol stabilized by methyl groups even as methylation stabilizes the parent sugar. Acidification, bringing the iodine absorption down to 100%, reflects a de-enolization.

Similarly, tetramethylmannose[3] was shown to yield only tetramethylglucose under the same conditions, with the same evidence of enolization and de-enolization. In both cases the corresponding unmethylated sugars, glucose and mannose, respectively, were shown to produce fructose with some saccharinic acid, but no stable intermediate enol under the same conditions.

If the foregoing considerations are correct, it follows that if the hydroxyl on the second carbon in a methyl glucose remains unmethylated, the 1,2-enediol resulting from alkali treatment would also be unmethylated and therefore capable of forming a ketose according to the accepted explanation of the shifting hydrogen atom of an enol. Furthermore, if only the hydroxyl on the third carbon atom in such a methylated glucose were methylated, the 2,3-enediol could form, in addition to the 1,2-enediol, but further enolization would be blocked. The 2,3-enol so formed would be a monomethyl-enediol and therefore its stability under the conditions as evidenced by iodine absorption would become a point of interest. If the methylated ketose thus formed should lend itself to isolation, the

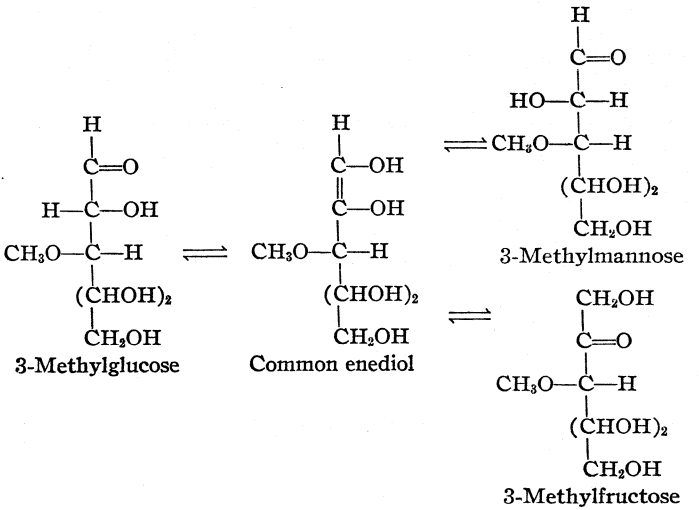
[1] Abstracted from a dissertation submitted by Donald J. Loder to the Graduate School of Northwestern University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Wolfrom with Lewis, THIS JOURNAL, **50**, 837 (1928).

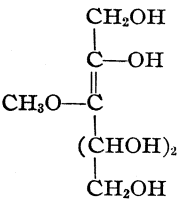
[3] Greene with Lewis, *ibid.*, **50**, 2813 (1928).

method suggests a source of new methylated ketoses and aldoses not now known, by dilute alkali conversion of the complementary methylated aldoses and ketoses.

3-Methylglucose offered the desired structure. The 3-methylfructose[4] to be expected is a well-defined compound. With the exception of the desired methyl group on the third carbon atom, 3-methylglucose most nearly resembles the parent glucose of any possible methylated sugar. Sobotka[5] has already given evidence from oxidation that the single methyl group blocks complete enolization of the sugar. The following system is therefore to be expected when 3-methylglucose is treated with dilute alkali




The above enediol group being unmethylated like that from glucose, should not yield a high iodine absorption on equilibration of the monomethylglucose with alkali. Should enolization proceed down the carbon chain to form the possible 2,3-monomethyl-enediol (A), the high iodine absorption of a stable methylated enol would be expected. Therefore, a normal iodine consumption of the equilibrated solution before acidification would give evidence that the 2,3-monomethyl-enediol did not form.



When 3-methylglucose was treated with lime water under the conditions of conversion used throughout these studies it was found to behave very much like glucose itself save that equilibrium was reached in forty-seven hours whereas in the case of glucose the changes are not complete at the end

[4] Ohle and Koller, *Ber.*, **57**, 1571 (1924).

[5] Sobotka, *J. Biol. Chem.*, **69**, 267 (1928).

of one hundred sixty-three hours. Abnormal iodine absorption was not found from which it is concluded that lime water is not a sufficiently strong alkali to cause enolization beyond the carbon atoms 1 and 2. That is, the stable 2,3-monomethyl-ene-diol was not present. Some methanol was split off, probably incident to a small amount of saccharinic acid formation. Excess of lime and higher temperatures, or stronger alkalies at a temperature of 35°, caused rapid and extensive changes in 3-methylglucose with considerable loss of methanol. With lime water at 35° the drop in $P_H$ and the loss of methoxyl corresponded roughly to the saccharinic acid formed, namely, 3.5% of the original sugar as calculated from the titration of the reaction mixture after removal of calcium ions. The aldohexose content as determined by iodimetry was 64.1%. This, with the 3.5% of saccharinic acid, would indicate that 32.4% of the original sugar must have been transformed into ketohexoses. $[\alpha]_D^{20}$ of the mixture calculated on the assumption that only 3-methylglucose and 3-methylfructose were formed was +15.9°. The observed value was 15.6°. The fact that the calculated value checks closely with that observed, when it is further known that saccharinic acid formation took place to the extent of 3.5% of the original sugar, suggests the presence of a small amount of a low rotary sugar, probably 3-methylmannose. This was not isolated. In any event the iodimetric value and the specific rotation of the mixture indicate that the products of alkali conversion are mainly 3-methylglucose and 3-methylfructose. It is noteworthy that glucose yields glucose and fructose in the same proportion under the same conditions.[2] The resemblance between the behavior of 3-methylglucose and glucose as well as the greater speed of conversion of 3-methylglucose are shown in Fig. 1.

TABLE I

RATE OF TRANSFORMATION OF 3-METHYLGLUCOSE INTO 3-METHYLFRUCTOSE

| Time in hours | $[\alpha]_D^{20}$ | Per cent. of glucose changed to fructose |
|---|---|---|
| .. | 55 | 0 |
| 12 | 25.5 | 25.2 |
| 17 | 23.2 | 28.4 |
| 34 | 17.3 | 35 |
| 47 | 15.9 | 35.1 |
| 288 | 15.6 | 32.4[a] |

[a] Final value corrected for saccharinic acids.

From the reaction mixture 3-methylfructose was isolated in pure crystalline form. This establishes that the methyl group in monomethylfructose obtained by the methylation and hydrolysis of diacetone-fructose is located in the same position as in monomethylglucose. This latter has been proved to be on the third carbon atom but the position of the methyl in monomethylfructose has rested on the likeness of the osazones of the

two monomethyl sugars. However, the variation in melting points of 3-methylglucosazone[6] has lent uncertainty to the proof.

3-Methylglucose was separated from the reaction mixture as the calcium salt of 3-methylgluconic acid and identified as the brucine salt. A small fraction of brucine salts showed very different properties from those of 3-methylgluconate, indicating the presence of small amounts of other acids, probably saccharinic and 3-methylmannonic.

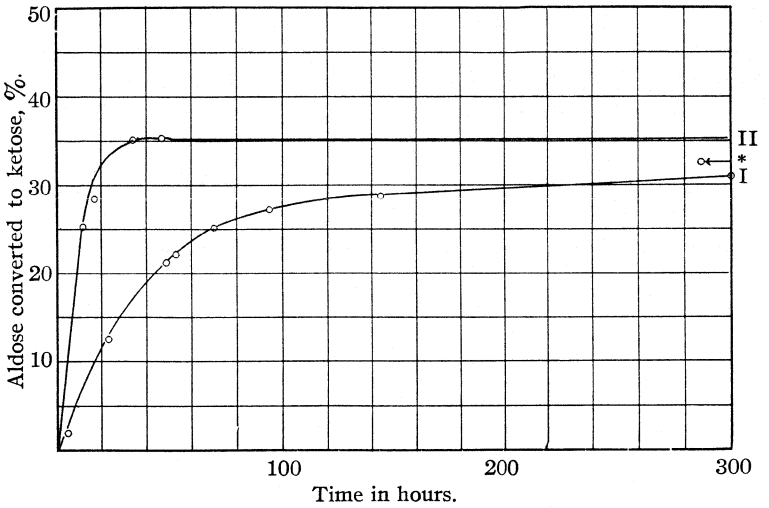



Fig. 1.—Comparison of the rates of transformation of glucose (I) and 3-methylglucose (II). * Final value on 3-methylglucose corrected for saccharinic acids.

## Experimental Part

**Preparation of 3-Methylglucose. Diacetone-glucose.**—The method finally employed in the preparation of diacetone-glucose was a combination of various methods, principally those of P. A. Levene,[7] Karl Freudenberg[8] and H. Ohle.[4] To 10 liters of pure acetone contained in a 12-liter flask was added with rapid mechanical stirring 100 cc. of concd. sulfuric acid. Five hundred grams of crystalline glucose[9] was then added and the mixture stirred very rapidly with moisture excluded for about forty-eight hours. Without removing the undissolved sugar, the acid was neutralized by passing a stream of dry ammonia gas into the mixture until the solution was faintly alkaline to litmus, meanwhile stirring rapidly and cooling under running water. The

[6] (a) Irvine and Hynd, *J. Chem. Soc.*, **95**, 1220 (1909); (b) Irvine and Scott, *ibid.*, **103**, 573 (1913); (c) Anderson, Charlton, Haworth and Nicholson, *ibid.*, **132**, 1337 (1929); (d) Freudenberg and Hixon, *Ber.*, **56**, 2126 (1923).

[7] Levene and Meyer, *J. Biol. Chem.*, **57**, 317 (1923); Levene and Raymond, *ibid.*, **83**, 619 (1929).

[8] Freudenberg and Ivers, *Ber.*, **55**, 933 (1922).

[9] The product used is prepared on a commercial scale by the Corn Products Refining Co. and sold under the trade name "cerelose."

precipitate was then filtered with suction and washed with a little acetone. The acetone was evaporated rapidly from the solution under diminished pressure and the residue finally heated on the boiling water-bath for half an hour. The residue, which usually became solid, was repeatedly extracted with boiling ligroin (b. p. 80–90°). The extracts were then allowed to cool in the refrigerator and the crystalline mass filtered and washed with a little ligroin. The weight of the crude, colorless, diacetone glucose was generally about half the weight of the sugar taken. The crude material was dissolved in the minimum quantity of cold benzene and the resulting solution washed twice with 6 *N* sodium hydroxide solution and twice with water. The benzene was then evaporated under diminished pressure, the temperature being so regulated as to avoid crystallization, the last of the benzene being removed on a boiling water-bath under diminished pressure. In case crystallization had taken place, the residue was heated until complete solution resulted and about ten volumes of boiling ligroin (b. p. 80–90°) added. The solution, while still hot, was nucleated with a crystal of diacetone-glucose and the mixture shaken gently during the cooling, crystallization being completed in the refrigerator. The crystalline mass was filtered with the aid of suction, washed with low boiling petroleum ether and air dried. The product prepared in this way was pure white and melted correctly at 109–111°; reported, 110–111°.[10]

**Diacetone-3-methylglucose.**—The method developed by Freudenberg[11] for methylating diacetone sugars was used with only slight modification. In a 3-liter distilling flask were placed 569 g. (2.15 moles) of pure diacetone-glucose and 2.5 liters of dry benzene. The solution was then added with cooling to 70 g. of finely divided sodium in a 3-liter flask and the mixture allowed to stand overnight under a reflux condenser, care being taken to exclude air. The next morning the mixture was heated under a reflux condenser for about an hour and allowed to stand for three hours with frequent shaking. The solution was then transferred to a dry 3-liter distilling flask with the aid of suction, great care being taken to exclude moisture. The sodium residue was washed with dry benzene and the washings added to the main solution. Most of the benzene was then removed by distillation under diminished pressure at 50°. To the cooled, viscous solution was then added 600 g. of methyl iodide, and the mixture shaken thoroughly and cooled from time to time. On standing for two days the whole mass solidified. The precipitated sodium iodide was dissolved by adding 600 cc. of water and some benzene to the reaction flask. The benzene layer was separated, washed once with water, and dried with anhydrous potassium carbonate. The remaining benzene was removed by distillation from a one-liter Claisen flask and the crude diacetone-glucose fractionated. The product boiled at 103–106° with a bath temperature around 123° and a pressure of 4 mm. To the distilled diacetone derivative were added 28 g. of methyl iodide and 23 g. of silver oxide. The mixture was then warmed on the water-bath overnight. The product was separated from the silver oxide and redistilled: yield, 500 g., or 84% of the theoretical amount.

**3-Methylglucose. Hydrolysis of Diacetone-3-methylglucose.**—In a 3-liter flask was placed 1600 cc. of an equal mixture of methyl alcohol and water containing 17.6 g. of concentrated sulfuric acid. To this was added 100 g. of pure diacetone-3-methylglucose and the mixture heated on the water-bath for three hours. The acid was then neutralized with barium carbonate and the filtered solution evaporated under diminished pressure to a thick sirup which, after the addition of an equal volume of methyl alcohol, was nucleated with a crystal of 3-methylglucose. When the crystallization was practically complete, a little acetone was added and the mixture left in the refrigerator overnight. The crystals were filtered with the aid of suction, washed with a little

[10] E. Fischer and C. Rund, *Ber.*, **49**, 93 (1916).

[11] Freudenberg and Hixon, *ibid.*, **56**, 2119 (1923).

methyl alcohol, and dried *in vacuo* over sulfuric acid: yield, 54 g., or 76% of the theoretical amount; $[\alpha]_D^{25}$ +55.2° in sixteen hours ($\alpha$ = +4.48°, 2 dcm., $c$ = 4.06 in water). The 3-methylglucose used finally in the equilibration experiment was carefully dried at 90° *in vacuo* over phosphorus pentoxide.

*Anal.* Calcd. for $C_7H_{14}O_6$: $OCH_3$, 15.95. Found: $OCH_3$, 15.90.

$[\alpha]_D^{20}$ +74.0°, initial; $[\alpha]_D^{20}$ + 55.0°, final ($\alpha$ = +4.70°, 2 dcm., $c$ = 4.27 in water); recorded,[12] $[\alpha]_D^{17}$ + 104.3°, initial, and 55.3° after 19.5 hours.

**Preparation of 3-Methylfructose. α-Diacetone-fructose.**[4]—A mixture of 225 g. (1.25 moles) of fructose (Pfanstiehl 90%) and 4500 cc. of acetone containing 10 cc. of concentrated sulfuric acid was stirred rapidly for about thirty-six hours, when complete solution had usually taken place. The acetone solution was then made slightly alkaline by passing a stream of dry ammonia gas into it with rapid stirring. The filtered solution was evaporated under diminished pressure at 40° to dryness. The residue was extracted with 1 liter of ether, the ether extract washed with 300 cc. of 6 *N* sodium hydroxide solution and dried with 100 g. of anhydrous potassium carbonate. The ether solution was then concentrated under diminished pressure to a volume of about 200 cc., cooled in the refrigerator, the resulting crystalline mass filtered with the aid of suction and washed with a little ether. It was then heated to boiling with 500 cc. of petroleum ether (b. p. 63–93°). After the mixture had stood in the refrigerator overnight the product was filtered, washed and dried: yield, 102 g., or approximately 30% of the theoretical amount; $[\alpha]_D^{25}$ −159° ($\alpha$ = −4.36°, 1 dcm., $c$ = 2.74 in water), reported, $[\alpha]_D$ −162.8°.[13]

**Preparation of α-Diacetone-3-methylfructose.**—The method used in methylating the diacetone-fructose is that of Freudenberg and Hixon[11] with slight modifications. To 500 cc. of dry benzene in a 1-liter distilling flask was added 25 g. of finely divided sodium metal. To this mixture was added in three portions 100 g. of diacetone fructose. It was necessary to cool the flask somewhat. The next morning the benzene was removed by distillation under diminished pressure at 35–40° and to the sirupy residue was added with shaking 110 g. of methyl iodide. The mixture stood for forty-eight hours, when 500 cc. of absolute ether was added and the solution decanted from the sodium into a 1-liter flask. The ether solution was filtered with considerable difficulty and the sodium iodide residue washed with ether and finally extracted with 200 cc. of benzene. (In later experiments the difficulty of filtering was avoided by decanting the benzene solution into a dry distilling flask with the aid of suction, thus separating the sodium. Water was then added to the ether solution to dissolve the sodium iodide. Ordinary ether may be used here.) The ether was removed by distillation, using diminished pressure finally. During the distillation the compound crystallized. After standing in the refrigerator overnight the crystals were filtered, washed with a little ether and dried; weight, 87 g. The filtrate was evaporated with the benzene extract under diminished pressure, taken up in a little absolute ether and placed in the refrigerator; weight, 10 g.; total yield, 97 g., or 92% of the theoretical; m. p., 114–115°; reported, 114–115°—(Ref. 11, p. 1343).

**Preparation of 3-Methylfructose. Hydrolysis of α-Diacetone-3-methylfructose.**—To 1200 cc. of an equal mixture of water and methyl alcohol containing 13 g. of concentrated sulfuric acid was added 60 g. of α-diacetone-3-methylfructose and the mixture heated for two hours on the steam-bath. The acid was neutralized with barium carbonate and the filtered solution evaporated under diminished pressure to a sirup.

[12] Anderson, Charlton and Haworth, *J. Chem. Soc.*, **132**, 1329 (1929).

[13] Fischer, *Ber.*, **28**, 1164 (1895); Irvine and Hynd, *J. Chem. Soc.*, **95**, 1223 (1909); Irvine and Patterson, *ibid.*, **121**, 2160 (1922).

The sirup was concentrated twice with 200 cc. of methyl alcohol. To the sirup was added 200 cc. of acetone, part of which was then removed by distillation. Crystallization was completed by the addition of a little dry ether. The product was filtered, washed and dried in the usual way: yield, 35 g., or 82% of the theoretical amount.

$[\alpha]_D^{20}$ −54.0° in twelve hours ($\alpha$ = −4.52°, 2 dcm., $c$ = 4.18 in water); reported $[\alpha]_D^{20}$ −53.5° ($c$ = 0.92).[13]

**Preparation of the Alkaloidal Salts of 3-Methylgluconic Acid.**—In a 1-liter florence flask 19.4 g. of 3-methylglucose was dissolved in 750 cc. of water and oxidized according to the method of Hudson and Isbell.[14] The oxidized solution was finally extracted six times with 100-cc. portions of chloroform, made up to a volume of 1000 cc. and split into two equal portions, one to be used in preparing the cinchonine salt and the other the brucine salt of 3-methylgluconic acid. One-half of the oxidation solution was evaporated in a tared 500-cc. flask to a gum which was dried by heating under diminished pressure at 110° for two hours. The weight of the gum was 9.5 g.; theoretical weight, 9.6 g. $[\alpha]_D^{25}$ +38.4° ($\alpha$ = +0.78°, 1 dcm., $c$ = 2.03 in water). The equivalent weight was 206, the calculated equivalent weight of the lactone being 192 and of the acid 210. The lactone could not be crystallized and did not give a crystalline phenylhydrazide.

The gum (9.16 g.) was dissolved in 200 cc. of water, 18 g. of recrystallized brucine added and the mixture heated on the water-bath until complete solution took place. The water was then evaporated under diminished pressure until a thick sirup was obtained to which 200 cc. of absolute ethyl alcohol was added and the mixture placed in the refrigerator. The crystals were filtered with the aid of suction, washed with absolute alcohol and air dried; yield, 21.7 g., or 78% of the theoretical amount. The product was recrystallized from a 50% water–alcohol mixture and dried over phosphorus pentoxide *in vacuo* at 98°; m. p. 146–148°, heated from 135° at 3° per min.; $[\alpha]_D^{25}$ −16.7° ($\alpha$ = −1.68°, 2.2 dcm., $c$ = 4.56 in water).

*Anal.* Calcd. for $C_{23}H_{26}N_2O_4 \cdot C_7H_{14}O_7$: N, 4.63. Found: N, 4.64.

The second half of the oxidized glucose solution was heated on the steam-bath with 18 g. of pure cinchonine for ten hours with rapid mechanical stirring, at the end of which time the solution had taken up 11.9 g. of cinchonine of the theoretical 14.7 g. The filtered solution was evaporated under diminished pressure to a sirup which was dissolved in 300 cc. of absolute alcohol and the small precipitate removed by filtration. The filtrate was evaporated again to a sirup which was taken up in a small amount of absolute alcohol and allowed to crystallize in the refrigerator. The product was separated by filtration, washed with acetone and dried; yield, 17.5 g., or 70% of the theoretical amount. The salt was recrystallized once from absolute alcohol. The recrystallized product was not completely soluble in water, indicating that the absolute alcohol had reacted to some extent with the salt. The insoluble substance was separated by dissolving the salt in 30 cc. of water and filtering. The filtrate was evaporated under diminished pressure to a small volume and placed in the refrigerator to crystallize. The crystals were filtered and dried, first in the air and then at 76° *in vacuo* over phosphorus pentoxide. The product, although crystallizing readily, did not possess a definite melting point, but decomposed with evolution of gas at temperatures depending on the rate of heating; $[\alpha]_D^{25}$ +113° ($\alpha$ = +6.24°, 1 dcm., $c$ = 5.51 in water).

**Preliminary Study of Methods of Identification and Separation.**—It was found that Cajori's[15] method for determining aldoses in the presence of ketoses by iodimetry was

[14] Hudson and Isbell, THIS JOURNAL, **51**, 2225 (1929).

[15] Cajori, *J. Biol. Chem.*, **54**, 617 (1922).

applicable to mixtures of 3-methylglucose and 3-methylfructose. 3-Methylglucose is rapidly oxidized by excess 0.1 *N* iodine in the presence of sodium carbonate while 3-methylfructose is but slowly attacked by the reagent under the same conditions. The rates of oxidation are about equally affected by change in temperature. At 25°, under the conditions employed, 3-methylglucose was 95% oxidized in thirty minutes. The rate of oxidation from that point was very slow. 3-Methylfructose was attacked more rapidly when alone, than in the presence of 3-methylglucose. At the end of thirty minutes, iodine corresponding to 1.6% aldose was used. A thirty-minute period at 25° was adopted. To apply the method to mixtures of 3-methylglucose and 3-methylfructose of different concentrations, it was necessary to establish an empirical relation between the iodine consumed and the relative quantities of the two sugars present. To do this it was only necessary to employ samples of mixtures of the two sugars under the same conditions and using the same total sugar concentration. The percentage of aldose shown by the amount of iodine used was then plotted with the actual concentration of the two sugars. The experiment was carried out in the following way. Solutions of 3-methylglucose and 3-methylfructose, each containing 5 mg. per cc., were prepared and mixed accurately in varying proportions, the total volume always being 20 cc. and containing a total of 0.1 g. of the two sugars. To the 20 cc. of sugar solution contained in a 500-cc. glass-stoppered flask was added 25.00 cc. of 0.09135 *N* iodine solution and 6 cc. of 15% sodium carbonate solution. The mixture was shaken and placed in the dark for exactly thirty minutes at 25°. The carbonate was then neutralized by adding a slight excess of 10% sulfuric acid. The excess iodine was then titrated with 0.05591 *N* sodium thiosulfate solution. The data obtained are shown in Table II.

TABLE II

OXIDATION OF MIXTURES OF 3-METHYLGLUCOSE AND 3-METHYLFRUCTOSE

| Thiosulfate, 0.05591 *N* | | | | | Iodine, 0.09135 *N* | | |
|---|---|---|---|---|---|---|---|
| 3-Methyl-glucose soln., cc. | 3-Methyl-fructose soln., cc. | Blank | Thiosulfate, cc. | Difference | 3-Methyl-glucose from $I_2$, mg. | 3-Methyl-glucose present, mg. | 3-Methyl-fructose present, mg. |
| 20 | 0 | 40.90 | 23.25 | 17.65 | 95.7 | 100 | 0 |
| 18 | 2 | 40.90 | 24.90 | 16.00 | 86.8 | 90 | 10 |
| 16 | 4 | 40.90 | 26.60 | 14.30 | 77.6 | 80 | 20 |
| 15 | 5 | 40.90 | 27.50 | 13.40 | 72.8 | 75 | 25 |
| 14 | 6 | 40.90 | 28.20 | 12.70 | 68.9 | 70 | 30 |
| 12 | 8 | 40.90 | 29.90 | 11.00 | 59.6 | 60 | 40 |
| | | | | | 1.6 | 0 | 100 |

These data are plotted in Fig. 2 and may be used for converting observed aldose content into actual aldose content when the conditions employed in preparing the chart are strictly adhered to in the determination. The application of the method to the equilibrated solution necessarily depends upon the assumption that only 3-methylglucose and 3-methylfructose are formed by the action of lime water, an assumption which is not strictly correct.

After a preliminary study of the separation of glucose and fructose by means of oxidation, formation of the calcium salt and solution of the fructose in alcohol, the method was applied to known mixtures of 3-methylglucose and 3-methylfructose. The residual sirup from the evaporated alcohol extracts easily yielded crystalline 3-methylfructose on inoculation but the lime salts of 3-methylgluconic acid were invariably high in calcium. Finally, by making the solution of 3-methylgluconic acid just alkaline to phenolphthalein with lime water, after neutralizing with calcium carbonate and

then discharging the color with oxalic acid and filtering, it was possible to get a lime salt of correct calcium content. This salt was thrown out of the concentrated neutralized oxidation mixture by the addition of twenty volumes of methyl alcohol followed by a like amount of acetone with vigorous stirring. A second precipitation was usually necessary to remove final traces of reducing monomethylfructose.

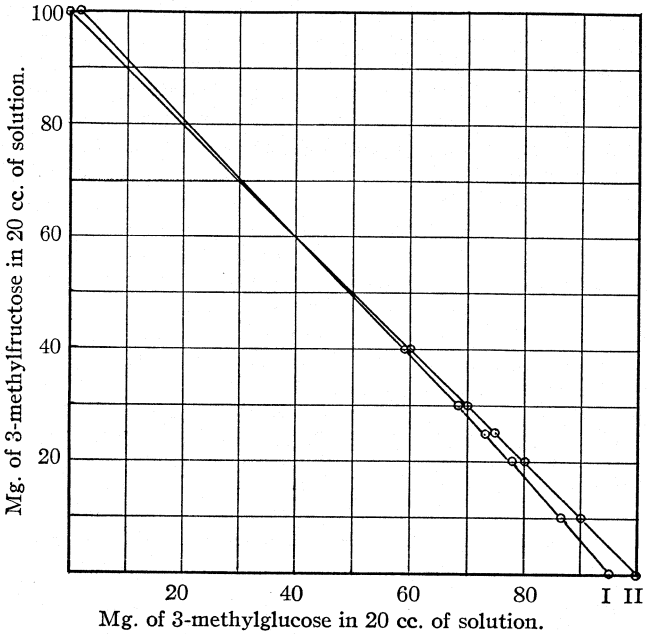



Fig. 2.—Reference curves for determining concentration of 3-methylglucose in the presence of 3-methylfructose: I, observed concentration; II, actual concentration. Concentration of total sugar, 5 mg. per cc.

**The Equilibration of 3-Methylglucose with Lime Water.**—Into a 500-cc. volumetric flask was weighed 97.06 g. of 3-methylglucose and the flask filled to the mark with clear lime water saturated at 35° (0.0407 *N*). The normality fell to 0.035. The solution was molar with respect to 3-methylglucose and of a density 1.06 at 35°. The flask was placed in a thermostat at 35° and the specific rotation and the aldohexose content determined. These gradually decreased until at the end of about forty hours a constant value was reached. The optical observations were made in a 2-dcm. jacketed tube at 20° on a 5% solution made acid to methyl orange. The equilibrium rotation was 15.6 at the end of 288 hours and the aldohexose content 64.1%. The methoxyl content was found to be 15.1% against a theoretical of 15.97%. The $P_H$ was 6.35 as determined by the quinhydrone electrode. The polarimetric data are recorded in Table III together with the specific rotation calculated from the iodimetric data, assuming that 3-methylglucose and 3-methylfructose are the only substances present.

The tabular data are shown graphically in Fig. 3. The close relation between the polarimetric data and the iodimetric data indicates that the main substances present in the reacting mixture at any time are 3-methylglucose and 3-methylfructose.

TABLE III

POLARIMETRIC DATA OF MOLAR 3-METHYLGLUCOSE IN 0.035 *N* CALCIUM HYDROXIDE SOLUTION AT 35°

| Time, hours | Observed $\alpha$ | $[\alpha]_D^{20}$ | $[\alpha]_D^{20}$ Calculated from iodimetric data |
|---|---|---|---|
| ... | .. | 55.0 | .. |
| 12 | 2.53 | 25.5 | 27.5 |
| 17 | 2.36 | 23.2 | 24.1 |
| 34 | 1.82 | 17.32 | 16.8 |
| 47 | 1.59 | 15.9 | 16.8 |
| 59 | 1.67 | 16.0 | 15.9 |
| 288 | 1.63 | 15.6 | 15.9 |

TABLE IV

IODIMETRIC DATA OF MOLAR 3-METHYLGLUCOSE IN 0.035 *N* CALCIUM HYDROXIDE SOLUTION

| Time, hours | Aldose, % | Ketose (by difference), % | $[\alpha]_D^{20}$ Calculated from iodimetric data |
|---|---|---|---|
| 12 | 74.8 | 25.2 | 27.5 |
| 17 | 71.6 | 28.4 | 24.1 |
| 34 | 65.0 | 35.0 | 16.8 |
| 47 | 64.9 | 35.1 | 16.8 |
| 59 | 64.1 | 35.9 | 15.9 |
| 288 | 64.1 | 35.9 | 15.9 |

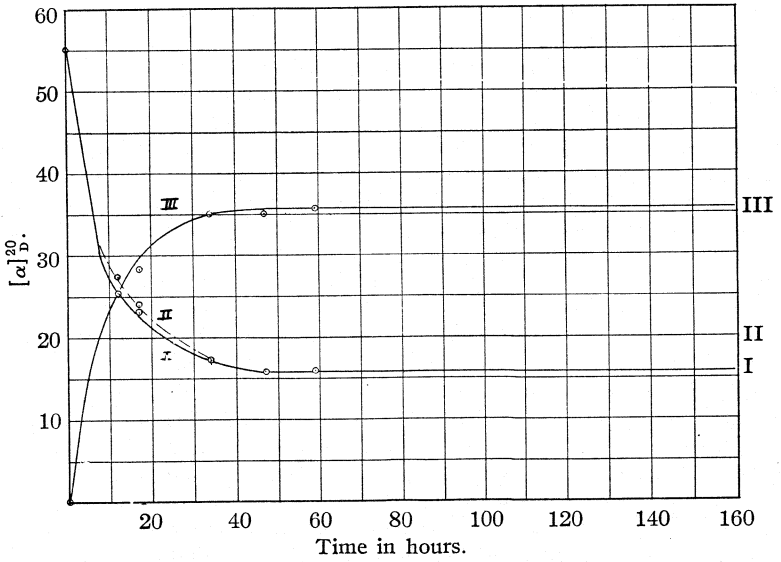



Fig. 3.—Interconversion of 3-methylglucose in dilute alkali: I, observed change in rotation; II, calculated change in rotation; III, percentage of 3-methylglucose transformed into 3-methylfructose.

The fall in $P_H$ indicated the formation of saccharinic acids. These were estimated as follows. To 51.81 g. of equilibrated solution, the original normality of which was 0.0351, was added the calculated amount of oxalic acid. The acids liberated corresponded to 3.46% of the original sugar transformed into saccharinic acid. If the calcium hydroxide originally present had all been neutralized by saccharinic acid formation, in accordance with the drop in $P_H$, the corresponding percentage of 3-methylglucose so transformed would have been 3.68%. Also, the loss of methoxyl corresponds roughly to the percentage of saccharinic acid found. Methyl alcohol was confirmed in the distillate.

In his study of the action of lime water on glucose at 35°, Wolfrom[2] isolated a small amount of mannose as the phenylhydrazone. In the present study, 3-methylmannose could not be identified, although the polarimetric and iodimetric data indicated that it should be present in small amounts. Moreover, the close resemblance in other respects between the action of lime water upon glucose and upon monomethylglucose supports this conclusion. The search was made more difficult by the unknown nature of 3-methylmannose. It seems reasonable to suppose that the specific rotation of 3-methylmannose would be close to that of mannose, or about 15°. The fact that the observed rotation of the equilibrated solution checked closely the rotation calculated from iodimetric data, assuming that only 3-methylglucose and 3-methylfructose were present, indicates that another optical body must have been present to offset the small amount of saccharinic acids present.

**Separation of the Reaction Mixture.**—In a 1-liter florence flask was placed 166 g. of the equilibrated solution containing 30.4 g. of products from which the lime had been removed as calcium oxalate. From the preliminary data the mixture, in terms of original sugar, contained about 64% of monomethylglucose and mannose, 32% of monomethyl ketoses and 3.5% of saccharinic acids. It was oxidized by the method of Hudson and Isbell[14] and the aqueous solution concentrated under diminished pressure to a volume of about 500 cc. To the cold solution was added gradually a suspension of freshly prepared pure calcium hydroxide until the neutral point of phenolphthalein was reached, then a clear solution of lime water was added slowly and the solution kept slightly alkaline for half an hour. After the addition of a drop of acetic acid to the solution, it was evaporated under diminished pressure to a volume of 30 cc. To the residue was added 500 cc. of methyl alcohol with vigorous mechanical stirring, then 400 cc. of acetone in the same manner. The calcium salts came out as a finely divided precipitate. The mixture was stirred rapidly for one hour longer. The lime salt was then filtered with suction onto a weighed filter, washed with methyl alcohol and dried *in vacuo* over sulfuric acid; yield, 22.7 g., or 94% of the theoretical 22.9 g. of calcium hexonate and 1.07 g. of calcium saccharinate. The salt, which showed a very slight reducing action toward Fehling's solution, was dissolved in 25 cc. of water in a 1-liter flask and reprecipitated with 500 cc. of methyl alcohol and 300 cc. of acetone, washed and dried; weight, 21.3 g., or 89% of the theoretical amount.

*Anal.* Calcd. for $(C_6H_{13}O_6COO)_2Ca$: Ca, 8.75. Found: Ca, 8.97.

Previous experience had shown the difficulty of avoiding basic salt formation under these conditions. A portion of the salt was fractionally precipitated, the first fraction showing 9.45% calcium and the second, 8.76. The second fraction showed $[\alpha]_D^{25}$ +12.9° ($\alpha$ = +0.99°, 2.2 dcm., $c$ = 3.46 in water).

In a 500-cc. flask was placed the remainder of the calcium salts, 17.85 g. To the hot solution of the salt in 200 cc. of water was added slowly a solution containing 4.91 g. of oxalic acid. The last of the calcium and oxalate ions was removed by adding small amounts of oxalic acid and calcium hydroxide until the solution showed the presence of both ions. The filtrate was evaporated under diminished pressure to a gum which

was then heated *in vacuo* at 95° for four hours; weight, 14.2 g., or 95% of the theoretical amount. The equivalent weight was 205 against a calcd. of 192 for 3-methylgluconic lactone; $[\alpha]_D^{25}$ + 46.1° initial and 31.8° final ($\alpha$ = +1.72°, 2.2 dcm., $c$ = 2.45 in water). A sample of acid gum from the oxidation of pure 3-methylglucose prepared in the same manner gave an equivalent weight of 206 and $[\alpha]_D^{25}$ +38.6° ($\alpha$ = +0.78°, 1 dcm., $c$ = 2.03 in water). The remainder of the gum, 13.0 g., was dissolved in 100 cc. of water and heated on the water-bath for four hours with 30 g. of recrystallized brucine. The resulting solution was extracted four times with 150-cc. portions of benzene, and the aqueous solution treated with decolorizing charcoal, filtered and evaporated under diminished pressure to a volume of about 50 cc. To this residue was then added 100 cc. of absolute alcohol. The mixture was allowed to crystallize in the refrigerator overnight. The crystals were filtered, washed thoroughly with absolute alcohol and dried; weight, 24.3 g., or 40.3% of the theoretical amount and melting at 148–150° when rapidly heated. A portion was recrystallized from dilute alcohol, and dried *in vacuo* over phosphorus pentoxide. It melted at 146–148° when heated from 135° at 3° per minute. The melting point of pure brucine 3-methylgluconate is 146–148°. There was no change in melting point on mixing the two; $[\alpha]_D^{25}$ −16.9° ($\alpha$ = −1.55°, 2.2 dcm., $c$ = 4.16 in water). The specific rotation of known brucine 3-methylgluconate under the same conditions was −16.7°. From the filtrate there was obtained with some difficulty 3.0 g. more of brucine salt, by adding slowly absolute alcohol and then acetone to the concentrated aqueous solution of the salt. The filtrate from this last treatment could not be induced to crystallize. It was, accordingly, converted to the cinchonine salt as follows. The residue was taken up in about 300 cc. of water and the brucine precipitated by adding a considerable excess of barium hydroxide. The dried brucine from the solution weighed 8.7 g. The alkaline filtrate was extracted three times with benzene and the barium precipitated from the aqueous extract as completely as possible with dilute sulfuric acid. The filtrate was heated on the steam-bath with 6.0 g. of pure cinchonine for ten hours with rapid mechanical stirring. The solution took up 4.3 g. of cinchonine. The filtrate was evaporated under diminished pressure to a sirup which was taken up in absolute alcohol and the evaporation repeated. The final residue was dissolved in 10 cc. of absolute alcohol and allowed to crystallize in the refrigerator. The product was filtered and washed with acetone; weight, 3.2 g. This was converted back to the brucine salt. There was obtained in this way, 3.2 g. more of pure brucine 3-methylgluconate, melting at 146–148°. There was obtained from the cinchonine salt mother liquor, 1.1 g. more cinchonine salt. This was also converted back to the brucine salt; weight, 0.9 g., melting at 140–142°. The second crop of impure brucine salt (3.0 g.) was dissolved in alcohol, the solution decolorized and reduced to a small volume. Failing to obtain crystals, the salt was thrown out by the addition of acetone; weight of dried salt, 1.5 g., melting at 125–135°. The final cinchonine salt residue was converted back to the brucine salt. An acid gum weighing 1.0 g. was obtained from these cinchonine salt residues. The brucine salt was very soluble in alcohol and was only partially thrown out by addition of acetone; weight of brucine salt, 1.7 g. All the filtrates from the brucine salt residues were combined and evaporated to dryness; weight of final brucine salt residue, 3.1 g., melting at 70–75°. The total weight of pure brucine 3-methylgluconate was 27.5 g., or 72% of the theoretical amount, based on the gum taken. In addition, there was a total of 7.2 g. of impure brucine salts. The total weight of brucine salts was 34.7 g., or 91% of the theoretical, based on the weight of the gum taken. Of the brucine salt residues, 6.3 g. was converted back to the acid gum, which was dried *in vacuo* over sulfuric acid at 80° for four hours. This gum showed an equivalent weight of 196 against the calculated 192 for 3-methylgluconic

lactone; methoxyl 10.7 against 16.15; $[\alpha]_D^{25}$ +53.5° initial and +34° final ($\alpha$ = +0.40°, 1 dcm., $c$ = 1.18 in water). These data indicate a mixture of demethylated acids believed to be saccharinic and methylhexonic.

The methyl alcohol–acetone filtrate from the lime salts containing the ketoses was evaporated under diminished pressure to a sirup. About 20 cc. of acetone was added and the solution again evaporated. This was repeated once more. The final sirup was nucleated with a crystal of 3-methylfructose and placed in the refrigerator overnight. Ether was then added a little at a time until the total volume was about 300 cc. The mixture was then filtered and the sugar dried, first in the air and then *in vacuo*, over sulfuric acid; weight, 8.5 g. The filtrate was concentrated and gave 0.45 g. more sugar, bringing the total yield up to 9.0 g. From the analytical data the theoretical yield of ketoses should be 9.86 g. The weight is, therefore, 91% of the theoretical amount.

From a sample of the ketose isolated from the equilibrated solution in the above way, was isolated $\alpha$-diacetone-3-methylfructose identical in properties with that obtained by methylating $\alpha$-diacetone-fructose. To this end the ketose was dissolved in acetone containing five drops of concentrated sulfuric acid in 100 cc. of solution and the mixture allowed to stand for four hours. The acid was neutralized with ammonia gas, the solution filtered and evaporated under diminished pressure. The crystalline residue was dissolved in 100 cc. of ether, the ether solution washed once with water, dried with anhydrous potassium carbonate, and reduced to 5 cc., whereupon the characteristic crystals of $\alpha$-diacetone-3-methylfructose separated. The washed, dried crystals melted at 114–115°; recorded, 114–115°.[13]

The osazone was prepared and recrystallized several times from water–alcohol mixtures. It melted at 175–177° and did not change on mixing with known 3-methylfructose osazone; recorded, 177–179°.[16] The final sugar residue which would not crystallize was recovered. It weighed 1.5 g. after thorough drying, $[\alpha]_D^{25}$ +12° ($\alpha$ = +0.15°, 1 dcm., $c$ = 2.45 in water). Only oily products resulted on attempting to convert the material to an osazone. The change of specific rotation of the sugar from the mixture with temperature agreed very well with that shown by pure 3-methylfructose.

TABLE V

COMPARISON OF CHANGE WITH TEMPERATURE OF SPECIFIC ROTATION OF SUGAR ISOLATED WITH THAT OF PURE 3-METHYLFRUCTOSE

| Temp., °C | $[\alpha]_D$ of sugar from mixture | $[\alpha]_D$ 3-Methylfructose |
|---|---|---|
| 20 | −53.9 | −53.5 |
| 38 | −43.0 | −42.7 |
| 45 | −40.0 | −38.5 |

A second attempt was made to separate the constituents of the mixture. In this experiment the procedure was exactly the same except that the acid was converted to the calcium salt by the use of calcium carbonate instead of calcium hydroxide. From 166 g. of the equilibrated solution containing originally 30.4 g. of 3-methylglucose and having a final composition of 64.1% of 3-methyl aldoses, 3.5% of saccharinic acid and 32.4% 3-methyl ketoses, in terms of the original sugar, there was obtained 20.9 g. of lime salts out of the theoretical 23.97 g., or 87% of the theoretical amount, and 9.0 g. of 3-methylfructose, $[\alpha]_D^{20}$ −54.5° ($\alpha$ = −5.33°, 2 dcm., $c$ = 4.89) out of the theoretical 9.86 g., or 91% of the theoretical amount.

The residue from the isolation of 3-methylfructose was evaporated under diminished

[16] Ref. 11, p. 1337.

pressure to a gum; weight, 3.5 g. This gum was acidic, 0.2271 g. neutralized 0.394 cc. of *N* base. The same weight (0.2271 g.) of 3-methylgluconic acid would neutralize 1.08 cc. of *N* base. This residue was free from inorganic material. The remainder of the residue, 3.3 g., was dissolved in 25 cc. of water and heated on the steam-bath with excess calcium carbonate. From the filtrate was obtained in the usual way 0.8 g. of calcium salt. The final sugar residue could not be induced to crystallize.

The isolation of the crude calcium 3-methylgluconate and pure 3-methylfructose in high yields served as a useful check on the polarimetric and iodimetric data. The properties of the calcium salt made it necessary to employ the alkaloidal salts for the isolation of the pure 3-methylgluconic acid derivative. The data obtained from the separation of the products from the mixture check with the conclusions reached from analytical data that the principal constituents of the equilibrated solution are 3-methylglucose and 3-methylfructose.

**Behavior of 3-Methylfructose in Lime Water Saturated at 35°.**—While it was known from the work of Wolfrom[2] and Greene[3] that molar solutions of glucose and fructose in 0.035 *N* calcium hydroxide solution give very different final specific rotations when allowed to stand at 35°, it was hoped that 3-methylglucose and 3-methylfructose, on account of their much greater speed of conversion, would reach the same final rotation, thus evidencing a true equilibrium. This was, however, not the case. The fact that 3-methylglucose and 3-methylfructose do not give the same equilibrium rotation makes the investigation of the latter a separate problem and demonstrates clearly that in the case of the monomethyl sugars the Lobry de Bruyn interconversion in lime water does not give rise to a true equilibrium.

The change of rotation of a molar solution of 3-methylfructose in 0.035 *N* calcium hydroxide solution kept at 35° is shown in the following table.

TABLE VI

POLARIMETRIC DATA OF MOLAR 3-METHYLFRUCTOSE IN 0.035 *N* CALCIUM HYDROXIDE SOLUTION

| Time, hours | $\alpha$ | $[\alpha]_D^{20}$[a] |
|---|---|---|
| 0 | .... | −53.0 |
| 16 | −5.49 | −27.8 |
| 21.5 | −5.08 | −26.2 |
| 29.5 | −4.25 | −21.9 |
| 48.5 | −4.25 | −21.9 |

[a] (1 dcm., $c$ = 19.4 in water.)

The equilibrium rotation corresponds to about 29% of 3-methylglucose, assuming that the only products are 3-methylglucose and 3-methylfructose. The equilibrium rotation of molar 3-methylglucose in lime water was +15.9°.

## Summary

1. The conversion of 3-methylglucose into 3-methylfructose with lime water at 35° confirms the recorded position of the methyl group in 3-methylfructose.

2. Experimental evidence is given in support of the enediol theory and the precise blocking of enolization by methyl groups.

3. The enediol of 3-methylglucose is shown to resemble that of glucose rather than that of tetramethylglucose.

4. The absence of a high iodine absorbing product in the reaction mixture when 3-methylglucose is treated with lime water at 35° is taken as evidence that the 2,3-monomethyl-enediol does not form.

5. When 3-methylglucose is treated with lime water at 35° to no further change, about 64% of the sugar consists of aldose and 32% is converted to 3-methylfructose. Indirect evidence is given for the formation of about 3.0% of saccharinic acid. The remainder consists of a mixture of partially demethylated hexoses.

6. At 35° in dilute alkali the methyl group in 3-methylglucose is slowly removed as methyl alcohol. At 100° under the same conditions the loss is rapid.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 684]

# A STUDY OF THE HYDROLYSIS OF CORN STARCH AND ITS AMYLOSES WITH REFERENCE TO THE PRODUCTION OF GENTIOBIOSE[1]

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When the starches are hydrolyzed by means of dilute acid or by enzymes the disaccharide, maltose may be isolated.[2] Its concentration in the solution passes through a maximum and then decreases.[3] With enzymes it is the only disaccharide that is produced and comes apparently directly by hydrolytic scission. For this and other reasons the maltose residue is considered to be a part of the carbohydrate structure of the starches.

Another diglucose sugar, however, has been identified recently in the solution from the hydrolysis of corn starch.[4] This sugar, gentiobiose, is a reducing $\beta$-glucoside, the link being at position 6 in contrast to maltose which is an $\alpha$-glucoside and linked at position 4. As isolated both are delta lactoles.

It is known that in the presence of mineral acids glucose will undergo condensation to form amorphous uncharacterized polysaccharides. The first such synthesis was reported by Fischer.[5] It is carried out by allowing a 20% solution of glucose in *concentrated hydrochloric acid* (37%) to stand for *fifteen hours to three days* at *room temperature*, or *lower*, and at atmos-

[1] An abstract of a dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, Columbia University.

[2] (a) For bibliography see Walton, "A Comprehensive Survey of Starch Chemistry," New York, 1928; (b) Lintner and Düll, *Ber.*, **28,** 1522 (1895); (c) v. Friedrichs, *Arkiv Kemi, Min. Geol.*, **5,** No. 2 (1913–1915).

[3] Rolfe and Defren, THIS JOURNAL, **18,** 869 (1896).

[4] Berlin, *ibid.*, **48,** 2627 (1926).

[5] Fischer, *Ber.*, **23,** 3687 (1890); **28,** 3204 (1895).

pheric pressure. The unfermentable residue of this reaction after purification by alcohol–ether precipitations from water solution, is a non-crystallizing sirup, which contains some reducing disaccharide, named Fischer's isomaltose. The material has frequently been confused with Lintner's[2a,b,6] isomaltose. The two products have nothing in common except that they give phenylosazones which have identical melting points[2c] and that both sugar mixtures are split by emulsin.[2c,7] The specific rotations of the free sugars[6a,7a] and of the osazones[8] differ widely. Further, the conditions under which Lintner's isomaltose is formed are such that condensation of glucose has been found negligible.[7a]

By acetylating the material prepared according to Fischer's directions, Berlin,[9] and at about the same time Georg and Pictet,[10] isolated gentiobiose octaacetate. The yield is low; about 2 g. of acetate per 100 g. of glucose is recovered, corresponding to 1% of the free disaccharide. Berlin also found that the mother liquors (hydrol) obtained from the commercial hydrolysis of corn starch after crystallization of the glucose, contained unfermentable material resembling Fischer's isomaltose, and that gentioacetate could be isolated from this after acetylation.[4] The yield corresponds to 5.7% of the solids in the mother liquor, or about 0.57% of the original starch.

Since the hydrolysis of corn starch to produce glucose, commercially, is carried out at 142–145° (3 atmospheres' pressure) in 0.16% hydrochloric acid, the conditions to which the newly liberated glucose is subjected are substantially different from those that obtain in the Fischer treatment of glucose. It is rather surprising, therefore, to find gentiobiose in both places. The nearest approach to an actual polysaccharide synthesis from glucose under acid concentrations which are at all similar to those in the starch hydrolysis was carried out by Scheibler and Mittelmeier.[11] They heated a 10% solution of glucose in 2.5% sulfuric acid for twelve hours on a water-bath and were able to isolate from the reaction mixture an osazone of approximately the same melting point as Fischer's isomaltosazone. Harrison[12] also prepared some material which he considered as isomaltose, by heating a solution of 500 g. glucose and 0.7 mole of hydrochloric acid in each liter of solution for forty-eight hours at 75°. These experiments were

[6] (a) Lintner and Düll, *Ber.*, **26**, 2533 (1893); (b) Pictet and Vogel, *Helv. Chim. Acta*, **12**, 700 (1929).

[7] (a) V. Friedrichs, *Arkiv. Kemi., Min. Geol.*, **5**, No. 4 (1913–1915); (b) Armstrong, *Proc. Roy. Soc.* (London), **B76**, 597 (1905).

[8] Article by Ling, "Enzymic Hydrolysis of Starches in Relation to Constitution," in Walton, Ref. 2a.

[9] Berlin, THIS JOURNAL, **48**, 1107 (1926).

[10] Georg and Pictet, *Helv. Chim. Acta*, **9**, 444, 612 (1926).

[11] Scheibler and Mittelmeier, *Ber.*, **24**, 301 (1891).

[12] Harrison, THIS JOURNAL, **36**, 586 (1914).

performed long before Berlin's work, so that there is no indication that gentiobiose was a constituent of the mixtures. While many so-called Fischer's isomaltoses have been made, the only similarity among them has been their non-fermentability and ability to form osazones. The physical properties of the sirups and the osazones obtained therefrom vary widely.

The disaccharide gentiobiose in the corn starch hydrolytic liquors may come from the condensation of glucose in acid media catalyzed perhaps by impurities[13] or from a direct hydrolytic scission of one of the amyloses that makes up the corn starch. It must be remembered in this connection that the two corn amyloses[14] are widely different in physical properties, the alpha (15%) being non-dispersable and carrying combined with it certain fatty acids[15] while the beta (85%) is pure carbohydrate. Even when the corn $\alpha$-amylose has had the fatty acid hydrolyzed away from it, the remaining carbohydrate is still non-dispersable and totally different from the corn $\beta$-amylose.

The present investigation involved a systematic study of the action of dilute hydrochloric acid, namely, 0.06 molar (equivalent to commercial concentration 0.16%) on glucose, whole corn starch, corn $\alpha$-amylose, corn $\beta$-amylose and on gentiobiose under conditions of concentration, time, temperature and environment that obtain during the commercial hydrolysis of corn starch.[16]

Wherever possible the gentiobiose was isolated as the octaacetate and weighed, but in the runs on small batches specific rotations, reducing values or osazone formation had to suffice. Details are given later.

**I. Materials.**—The glucose used was the usual anhydrous alpha glucose. Gentiobiose was made from gentian root and isolated as the beta octaacetate. Some of this latter substance was also supplied by the Bureau of Standards.

Air-dried, alkali washed, whole corn starch containing 11% moisture and the corn amyloses with about the same moisture content were prepared in sufficient amounts for the entire set of experiments.

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[13] Ebert, Newkirk and Moskowitz, U. S. Patent 1,668,308, May 1, 1928.

[14] Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

[15] (a) Taylor and Nelson, THIS JOURNAL, **42**, 1726 (1920); (b) L. Lehrman, "The Fatty Acids in Corn Starch and Synthesis of Corn Beta Amylose Palmitate," Columbia Dissertation, 1925.

[16] The commercial hydrolysis[13] consists in treating about 2300 gallons of a 12.5° Bé. starch suspension with 90 pounds of commercial hydrochloric acid in a copper autoclave, and blowing in steam at 40–45 pounds per sq. inch pressure. The conversion is usually run for thirty minutes after the steam pressure has become constant. It is claimed that the walls of the autoclave, and the soluble copper salts formed by the action of the hydrolyzing acid on them, act as catalysts for the condensation of glucose.[13] To diminish the amount of synthetic material formed, it is recommended that the hydrolysis be carried out in vessels lined with glass-enamel or a similar material.[13] Translated to laboratory conditions the above would be equivalent to 344 g. of starch in 1 liter of 0.06 molar hydrochloric acid at a temperature of 141 to 142°. Since the pressure in the autoclave becomes constant at about 110° [45 lb. per sq. inch], all time intervals were started from the moment of attainment of the temperature.

The amyloses were obtained according to the directions of Taylor and Beckmann;[17] 300 g. of corn starch was ground in a porcelain ball mill with 3900 g. of quartz balls for one hundred and sixty-eight hours. The starch was dispersed in water and the components separated by electrophoresis. The β-amylose was obtained by concentrating the clear supernatant solutions under reduced pressure and then precipitating the carbohydrate with alcohol. The α-amylose was considered free of β-amylose when two successive dispersions in fresh water yielded supernatant liquids which no longer gave a blue color with iodine. It was dried by heating in a vacuum oven at 60° until it contained about 11% moisture (see V) [about equilibrium moisture for starch in air during winter].

**II. Rate of Hydrolysis of Whole Corn Starch and Corn β-Amylose.**—Since any synthesis of gentiobiose from glucose would depend obviously on the amount of glucose present, it was thought advisable to make a preliminary study of the rate of hydrolysis of whole starch and β-amylose, both of which produce glucose. The change was followed by a fall in specific rotation during treatment at 141° with the hydrochloric acid.

3.440 grams of carbohydrate and 10 cc. of 0.06 molar hydrochloric acid were sealed in heavy-walled Pyrex test-tubes and placed in a glycerin bath. The latter was then heated so that it took thirteen minutes to reach 110°, fifteen minutes more to reach 141°, where it was kept constant. At the stated intervals after the attainment of 110°, samples were removed and chilled in cold water to stop the reaction. The solutions were filtered and diluted to about 50 cc. Rotations were obtained in a 2-dm. tube with the green mercury line $\lambda = 5461$ Å. They were converted to the sodium D line by multiplying by the factor[18] 0.849. The weight of the dissolved material was determined by evaporating 10-cc. portions to dryness on ignited sand and drying for three hours at 110°.

The results of these experiments are given in Table I.

TABLE I

THE RATE OF HYDROLYSIS OF WHOLE STARCH AND β-AMYLOSE

| Time in minutes after reaching 110° | Whole starch $[\alpha]_D^{25}$ | β-Amylose $[\alpha]_D^{25}$ |
|---|---|---|
| 10 | 151 | 147 |
| | 149 | 149 |
| 15 | 120 | 104 |
| 20 | 69.0 | 63.1 |
| | 76.0 | 70.1 |

The nearer the specific rotation of these solutions approaches an $[\alpha]_D^{25}$ of 52.5°, the greater is the glucose content.[3,19] Apparently the concentration of glucose during most of the reaction is greater for β-amylose than for whole starch.

Later experiments on a larger scale show that at the end of a thirty-minute period the glucose content of a hydrolyzed β-amylose and whole starch solution are practically identical, the $[\alpha]_D^{25}$ being approximately

[17] Taylor and Beckmann, THIS JOURNAL, **51**, 294 (1929).

[18] Taylor and Walton, *ibid.*, **51**, 3431 (1929).

[19] Nanji and Beazeley, *J. Soc. Chem. Ind.*, **45**, 215T (1926).

62°. By extending the treatment to forty-five minutes other factors enter such as destruction of the glucose, etc.

**III. Treatment of Corn α-Amylose, β-Amylose and Glucose with 0.06 Molar Hydrochloric Acid.**—It is obvious from the results given under II that whole corn starch hydrolyzes less readily than the corn β-amylose. As previously mentioned,[14,15] whole starch has in it 85% of β-amylose and 15% insoluble fatty acid containing α-amylose. The experiments in this part were designed to find out the condition of affairs in the solution after corn α-amylose by itself is treated as under II for thirty minutes. In order to cover all conditions, corn β-amylose admixed with the fatty acids in kind and amount found in the given weight of α-amylose were treated also. Finally, glucose was similarly treated. This was done because these impurities are reputed to cause side reactions, possibly condensations. In the latter two instances the concentrations of β-amylose and glucose were taken equivalent both to the amount of α-amylose and of β-amylose as it occurs in the whole starch used in experiments under part II.

The time was again measured from the moment the bath reached 110°. Data from these experiments are found in Table II.

TABLE II

SPECIFIC ROTATION OF SOLUTION OF AMYLOSE AND GLUCOSE AFTER THIRTY MINUTE TREATMENT WITH 0.06 MOLAR HYDROCHLORIC ACID

| Expt. | Material | Ref. | Concn. equiv. to | $[\alpha]_D^{25}$ |
|---|---|---|---|---|
| 1 | α-Amylose | *a* | 15% starch | 49.4 |
| 2 | α-Amylose | | 15% starch | 50.6 |
| 3 | α-Amylose | *b* | 15% starch | 47.4 |
| 4 | β-Amylose | *c* | 15% starch | 60.6 |
| 5 | β-Amylose | | 15% starch | 59.5 |
| 6 | Glucose | *d* | 15% starch | 61.2 |
| 7 | Glucose | | 15% starch | 56.7 |
| 8 | β-Amylose | *e* | 85% starch | 61.4 |
| 9 | β-Amylose | | 85% starch | 61.1 |
| 10 | Glucose | *f* | 85% starch | 59.6 |
| 11 | Glucose | | 85% starch | 58.6 |

References: (*a*) 0.52 g. in 10 cc., (*b*) 12.9 g. + 250 cc. in autoclave, (*c*) 0.26 g. in 5 cc. + 8 mg. of mixed fatty acids, (*d*) 0.26 g. glucose + 5 cc. acid + 8 mg. fatty acid, (*e*) 1.46 g. + 5 cc. acid + 8 mg. fatty acid, (*f*) 1.46 g. glucose + 5 cc. acid + 8 mg. fatty acid. The fatty acids were added to the material in a chloroform solution and the solvent evaporated.

The intermediate scission products occurring in the hydrolysis of β-amylose have specific rotations greater than equilibrium glucose. This has been noted also for whole starch (see II). However, corn α-amylose when hydrolyzed by itself free from the large amount of β-amylose that accompanies it in whole corn starch gives a solution of distinctly lower

specific rotation than glucose when the hydrolysis has reached the thirty-minute mark.

Gentiobiose has an $[\alpha]_D^{25}$ of 9.8° at equilibrium and this disaccharide is found in hydrolyzed whole corn starch solutions;[4] therefore, the low specific rotation of the hydrolyzed $\alpha$-amylose solution above is due probably to the presence of this sugar. Further, although the amounts are small, the solutions from all the hydrolyses of the corn $\alpha$-amylose were combined and heated with phenylhydrazine and acetic acid for one and one-half hours on a water-bath. The glucosazone formed was filtered off and the filtrate cooled. A small amount of yellow crystals, needles, separated and after recrystallization twice from hot water they had a m. p. of 170–172°, softening at 168°; reported for gentiobiosazone, 168–170° (Georg and Pictet),[10] 179–181° (Berlin).[9]

There is, therefore, strong presumptive evidence that the gentiobiose found here has its origin in the corn $\alpha$-amylose and is a direct scission product of part of that material.

**IV. Condensation of Glucose to Gentiobiose.**—In order to obtain larger amounts of material so that attempts could be made actually to isolate gentiobiose as its octaacetate if it were present, an autoclave capable of taking a 500-cc. porcelain beaker was employed. Here again the concentration was fixed so that the commercial runs could be simulated. In the hydrolysis of a given weight of starch to glucose there is an 11% increase in weight of solids due to the addition of water. Since the moisture content of the starch and its amyloses is about 10%, it is sufficiently precise for this work to consider equal weights of glucose, starch and the components as equivalent weights. Accordingly 172 g. of glucose in 500 cc. of 0.06 molar hydrochloric acid was heated for stated periods, the temperature being followed by a thermometer in a glass-covered well projecting into the solution and by the steam gage on the cover of the autoclave.

To obtain the steam for heating the charge, water (150 cc.) was placed in the bottom of the autoclave, which was heated with a Méker burner. The rate of heating was such that thirteen minutes were required to obtain a gage reading of 45 pounds. The temperature of the reaction mixture was then about 110°. This is the point as mentioned previously from which all reaction periods were timed. The burner was then regulated so that the pressure remained constant. The temperature continued to rise and reached its constant value of 141° in fifteen minutes. To stop the reaction the pressure was released through the safety valve, the beaker and its contents removed and the solution made neutral to methyl orange with sodium carbonate, cooled and diluted with water to a liter. In order to get rid of the glucose, 50 g. of starch-free bakers' yeast was added with 25 cc. of yeast juice as nutriment and the whole allowed to ferment at 37° for three days. At this time no glucosazone was found in test portions of the solution, showing that glucose was for practical purposes absent. Following further an adaptation of Berlin[4] and Brauns[20] the procedure was as follows. The

[20] Brauns, THIS JOURNAL, **49**, 3170 (1927).

solution was boiled, cooled to room temperature, neutralized with saturated barium hydroxide solution, filtered and simultaneously decolorized, by means of hot norite on a Büchner funnel. The residue was washed several times with hot water and the washings combined with the filtrate. This filtrate was evaporated *in vacuo* to a thick sirup and extracted under reflux for three hours with 600 cc. of absolute methyl alcohol. After standing overnight the alcoholic solution was filtered from the small amount of precipitate, the latter washed with absolute methyl alcohol and the combined washings and filtrate evaporated *in vacuo* to a sirup. The latter was acetylated by heating on a water-bath with six times its weight of acetic anhydride and one-half its weight of fused sodium acetate. When solution was complete, the reaction mixture was heated for an hour, then let stand overnight at room temperature, and subsequently poured into three liters of ice water. The insoluble residue, after washing in the beaker with fresh water to remove as much of the acetic acid as possible, was stirred with cold absolute methyl alcohol. The gentiobiose octaacetate remained undissolved. After standing in the cold for several days it was filtered and recrystallized from absolute methyl alcohol. One recrystallization was usually sufficient to yield a product of the correct melting point and mixed melting point with a sample from gentian root. β-Gentiobiose octaacetate of highest purity melts at 195–196°.[9,21] The samples isolated melted over one degree ranges in the interval 190–194.5°, most of them 192.5–193.5°. Mixed melting points never differed by more than one degree. The alcoholic solutions from which the crystals were separated were subsequently worked up according to Berlin's method for isolating the acetate from the crude acetylated non-fermentable residues. These solutions were evaporated to dryness and the residue taken up in ether. The resulting solution was washed with water until neutral, then with 3% sodium bicarbonate solution and finally with water until neutral again. The ether was evaporated, the residue dissolved in absolute methyl alcohol and seeded. No more than traces of the acetate, however, were ever isolated by this further treatment.

The results of these experiments are given in Table III.

TABLE III

CONDENSATION OF GLUCOSE TO GENTIOBIOSE WITH 0.06 MOLAR HYDROCHLORIC ACID

| Time of treatment in mins. | Yield of gentiobiose octaacetate in grams | Yield of gentiobiose in grams |
|---|---|---|
| 30 | 2.24 | 1.12 |
| 30 | 1.77 | 0.89 |
| 45 | 1.70 | .85 |
| 45 | 1.33 | .67 |

It is evident that glucose in the presence of dilute acid and at high temperatures (141°) condenses to give some gentiobiose. It must be borne in mind, however, that this gentiobiose is only a small part, 10–15%, of the entire non-fermentable residue. When, for example, an acetylated sirup after the removal of the gentiobiose octaacetate is saponified with aqueous barium hydroxide and the barium ion removed quantitatively as barium sulfate, the resulting solution has an $[\alpha]_D^{25}$ of 76.6°. This value is close to that frequently reported for Fischer's isomaltose, (v. Friedrich +72.8,[7] Ost +70,[22] Harrison +84.1°[12]) though Georg and Pictet[10] report a higher value +98.5°. The latter assume that the lower rotations are due

[21] Zemplén, *Z. physiol. Chem.*, **85**, 399 (1913).

[22] Ost, *Chem.-Ztg.*, **20**, 762 (1896).

to contamination with gentiobiose $[\alpha]_D^{25}$ +9.8°. The condensation of glucose to gentiobiose takes place apparently when there is a large amount of glucose present.

**V. Treatment of Gentiobiose with 0.06 Molar Hydrochloric Acid.**—That gentiobiose itself in the absence of glucose is hydrolyzed to glucose is shown in the following experiments. Weighed amounts of gentiobiose were added to the requisite amount of 0.06 molar hydrochloric acid and the mixture placed in Pyrex tubes which were sealed and heated for specified periods as under (II). Since the low rotations of these solutions made polarimetric observations of slight value, the course of the reaction was followed by titrating the carbohydrates by the Willstätter–Schudel method.[23] Five cc. of the neutral solutions were treated with excess $N/20$ iodine and double this volume of $N/20$ sodium hydroxide was then slowly added. The solutions were kept in the dark for twenty minutes, acidified with $N$ hydrochloric acid and the liberated iodine titrated with $N/40$ sodium thiosulfate. The iodine is a measure of the glucose and gentiobiose present, according to the reaction $RCHO + I_2 + 3NaOH = RCOONa + 2NaI + 2H_2O$. One mole of gentiobiose yields two moles of glucose. Hence the percentage hydrolysis can be calculated by the equation, $\% (R_1 - R_0)/R_0 \times 100$ where $R_0$ = cc. of iodine required by the unheated solution and $R_1$ = cc. required after heating for a specified time. The results are given in Table IV.

TABLE IV

HYDROLYSIS OF GENTIOBIOSE IN 0.06 MOLAR HYDROCHLORIC ACID

| Time in minutes after reaching 110° | Concentration of gentiobiose per 100 cc. 0.230 g. | 0.306 g. | 0.942 g. |
|---|---|---|---|
| 0 | 1.66% | 1.88% | ... |
| 15 | 53.3% | 65.6% | 80.90% |
| 30 | 100 + (decomp.) | 100 + (decomp.) | 100 + (decomp.) |

The minimum concentration of gentiobiose used corresponds to about the maximum isolated from the hydrolytic liquors. The values in excess of 100% hydrolysis show that decomposition, with the formation of more reducing substances, had occurred. In fact, these solutions were discolored. All values may also be slightly high due to over-oxidation[24] by the alkaline iodine.

We have seen that corn $\beta$-amylose upon hydrolysis (see II) under the conditions set forth gives according to the specific rotatory value of the solution the highest concentration of glucose early in the treatment. This condition ought to be conducive, in the light of experiments under III, to the maximum yield of gentiobiose via the synthetic route.

[23] (a) Willstätter and Schudel, *Ber.*, **51**, 780 (1918); (b) Goebel, *J. Biol. Chem.*, **72**, 801 (1927).

[24] Kline and Acree, *U. S. Bur. Standards J. Research*, **5**, 1063 (1930).

Whole corn starch which gives less glucose (see II) early in the treatment, again according to the specific rotation, would be expected to be a less fertile source of gentiobiose by synthesis.

**VI. Hydrolytic Liquors of Whole Corn Starch and its Amyloses.**—In these experiments the autoclave was used as in (1V) and large samples (172 g.) were used in order to isolate if possible the gentiobiose itself. Since it took over a year to collect sufficient $\beta$-free $\alpha$-amylose the experiment could not be duplicated and unfortunately only one period of treatment could be tried.

The results of these runs show that whole corn starch after thirty minutes' treatment in the 0.06 molar hydrochloric acid will give a solution with an $[\alpha]_D^{25}$ of 62° from which 0.52 g. of gentiobiose may be isolated through the fermentation and acetylation procedure (see IV). A duplicate run gave 0.53 g. of gentiobiose. New samples treated for forty-five minutes gave solutions with an $[\alpha]_D^{25}$ of 58.2° and yielded 0.70 and 0.62 g. of gentiobiose, respectively.

$\beta$-Amylose after twenty minutes gave a solution with $[\alpha]_D^{25}$ of 67.7° and no gentiobiose, while three runs for a thirty-minute period gave solutions whose $[\alpha]_D^{25}$ ranged between 61.4 and 68° but yielded no gentiobiose. Duplicate runs for forty-five minutes gave solutions with an $[\alpha]_D^{25}$ of 56.4 and 57.8°, respectively, and no gentiobiose.

The only difference between whole corn starch and $\beta$-amylose is the 15% $\alpha$-amylose.

A thirty-minute treatment of corn $\alpha$-amylose showed that its hydrolysis when not dispersed in the $\beta$-amylose as when present in whole corn starch is slow, for the $[\alpha]_D^{25}$ of the solution is still 89.4° at the end of thirty minutes. Apparently scission of the amylose had taken place to give relatively large units of the dextrin type, for no gentiobiose could be isolated. The treatment of corn $\alpha$-amylose for a longer time is to be tried in the near future.

Although it is true that glucose will condense under these experimental conditions to give gentiobiose, yet the $\beta$-amylose which gives glucose in high concentration early in the treatment gives no gentiobiose. On the other hand, the slow hydrolyzing material such as the $\alpha$-amylose in whole starch or the $\alpha$-amylose itself gives the most gentiobiose. It seems then that when whole corn starch is hydrolyzed under three atmospheres' pressure with dilute hydrochloric acid, the major portion if not all of the gentiobiose formed comes directly by scission of the $\alpha$-amylose rather than through condensation of the glucose. The implications are interesting in connection with the make-up of corn $\alpha$-amylose for they point to the presence of a polysaccharide composed of gentiobiose units instead of maltose units in this fraction of corn starch.

**Acknowledgment.**—The authors wish to thank the Fleischmann

Yeast Company for generously supplying starch-free yeast and the Bureau of Standards for a sample of gentiobiose octaacetate.

## Summary

1. Glucose in 0.06 molar hydrochloric acid under three atmospheres' pressure condenses to give in thirty minutes about 1.5% gentiobiose.

2. Whole corn starch under the same conditions give some gentiobiose.

3. Corn $\beta$-amylose which constitutes 85% of the starch gives no gentiobiose.

4. Corn $\alpha$-amylose gives under the same hydrolytic conditions a solution of low specific rotation from which gentiobiose osazone has been isolated.

5. The gentiobiose found in solution from the hydrolysis of corn starch under the stated conditions seems to come from the direct scission of a polysaccharide in the insoluble $\alpha$-amylose fraction of corn starch rather than from condensation of glucose.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

# THE SYNTHESIS OF THYMOL, CHLOROTHYMOL AND HOMOLOGS OF THYMOL BY THE INTRAMOLECULAR REARRANGEMENT OF META-CRESYL ETHERS

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## Theoretical Part

The syntheses of thymol may be divided into two general classes; those which begin with benzene hydrocarbons as the starting point and those which start with *m*-cresol, condensing this phenol with acetone, isopropyl alcohol or propylene. The first class may be still further divided into those which start from *p*-cymene and those which begin with benzene itself.

Béhal and Tiffeneau[1] were the first to synthesize thymol starting with *p*-cymene. Since then a number of syntheses have appeared with this substance as the starting material. These methods depend upon the occupying of the position ortho to the methyl group with an amino group and then sulfonating. Finally the amino group is replaced by hydrogen and the sulfonic acid group by hydroxyl.[2] Austerweil and Lemray[3] have synthesized thymol starting from benzene using the standard methods.

[1] Béhal and Tiffeneau, *Bull. soc. chim.*, [4] **3**, 729 (1908).

[2] Andrews, U. S. Patent 1,306,512 (1919); Philips, *ibid.*, 1,332,680 (1920); Austerweil, British Patent 221,226 (1923); Bert and Dover, *Compt. rend.*, **182**, 634 (1926).

[3] Austerweil and Lemray, *Bull. soc. chim.*, **41**, 454 (1927).

The more direct manner of synthesizing thymol would be to condense *m*-cresol with isopropyl alcohol, propylene or acetone, reducing the product in the latter case. Such condensations have been tried using isopropyl alcohol, *m*-cresol and magnesium chloride or phosphoric acid.[4]

Acetone has been condensed with *m*-cresol in the presence of hydrochloric acid. The condensation product obtained was depolymerized by distillation and then reduced to give thymol.[5]

Inasmuch as in the condensation of allyl alcohol with *m*-cresol the dimer of *o*-isopropenyl-*m*-cresol can be obtained in excellent yield, the ultimate synthesis of thymol, upon reduction of this product, as in the foregoing case, ought to be possible.[6] In this group may be included the condensation of propylene with *m*-cresol in the presence of sulfuric acid.[7]

Successful attempts have been made to condense isopropyl alcohol with substituted *m*-cresols where the position para to the hydroxyl group has been blocked off. This removed the possibility of obtaining para isomers and the yields of substituted thymols are good. Isopropyl alcohol condenses with *m*-cresol sulfonic acid with the formation of thymol sulfonic acid. The sulfonic acid group is then removed by means of superheated steam.[8]

In a similar fashion, chlorothymol has been synthesized by the condensation of isopropyl chloride or isopropyl alcohol with chloro-*m*-cresol.[8c]

The present contribution proposes a different method for the preparation of thymol, substituted thymols and homologs of thymol. Isopropyl *m*-cresyl ether has been shown to rearrange with the formation of an isopropyl *m*-cresol which did not distil at constant temperature. The product has a strong odor of thymol, but its boiling point, acetic acid derivative (m. p. 141°) and other physical properties did not check too closely with that of thymol.[9]

In the rearrangement of unsaturated alkyl phenyl ethers and substituted diphenyl ethers by earlier investigators[10] *m*-cresol had not been dealt with. It was therefore necessary to study this reaction with a view toward the determination of the position taken up by the isopropyl group, so that the structure of this and similar compounds prepared by the rearrangement

[4] Mazzara, *Gazz. chim. ital.*, **12,** 505 (1882); Howard and Blagden, British Patent 200,151 (1922).

[5] Jordan, Schering Kahlbaum, British Patent 279,855, 279,857, 280,924 (1928); Canadian Patent 281,114, 281,120 (1928).

[6] Niederl, Smith and McGreal, THIS JOURNAL, **53,** 3390 (1931).

[7] Howard and Blagden, British Patent 214,866 (1923).

[8] (a) Badische Anilin und Sodafabrik, British Patent 186,202 (1921); (b) Gunther, U. S. Patent 1,412,937 (1922); (c) Raschig, Swiss Patent 127,035 (1927).

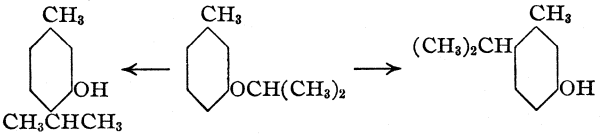
[9] Niederl and Natelson, THIS JOURNAL, **53,** 1928 (1931).

[10] Claisen, *Ber.*, **45,** 3157 (1912); *Ann.*, **418,** 69 (1919); *Z. angew. Chem.*, **36,** 478 (1923); Van Alphen, *Rec. trav. chim.*, **46,** 799 (1927); Kursanov, *J. Russ. Phys.-Chem. Soc.*, **48,** 1172 (1916).

of *m*-cresyl ethers could be ascertained. Twenty-five cc. of the liquid as obtained from the intramolecular rearrangement of isopropyl *m*-cresyl ether was fractionated with a special fractionating column. The fractions obtained, and the melting points of the corresponding acetic acid derivatives after one recrystallization, were shown to be

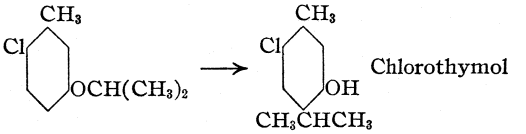
| | | |
|---|---|---|
| 231–235° | 5 cc. | 146° |
| 235–237° | 6 cc. | 132–137° |
| 237–244° | 12 cc. | 125° |

The derivative of the first fraction, that which boiled in the neighborhood of thymol, was identical with thymoxyacetic acid.[11] The highest fraction resembled more closely the product obtained by Mazzara[4] and Read.[12] The acetic acid derivative of the middle fraction did not melt sharply, but appeared to contain largely thymoxyacetic acid. Two recrystallizations of the acetic acid derivative of the original liquid obtained after rearrangement yielded a crystalline product which melted at about 141°, showing that thymoxyacetic acid is less soluble in water than its *p*-isomer and can be crystallized from it. It appears evident from the above that after rearrangement of the isopropyl *m*-cresyl ether a mixture was obtained which consisted of about 33% thymol and about 67% of the *p*-isopropyl-*m*-methylphenol.




Thymol *p*-Isopropyl-*m*-methylphenol

By blocking off the para position, a substituted thymol should be obtained in good yield. 4-Chloro-*m*-cresyl isopropyl ether was therefore rearranged and chlorothymol resulted in good yield.

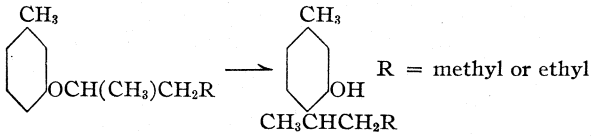



Because of the possible important antiseptic properties, homologs of thymol were prepared by rearranging secondary butyl and secondary amyl cresyl ethers. The liquid obtained from the rearrangement of *sec.*-butyl *m*-cresyl ether was fractionated and the portion which distilled constantly at lower temperatures was collected. The major portion of the product came over between 246–250°. The higher boiling portion was reserved for future study. The rearrangement of *sec.*-amyl *m*-cresyl ether

[11] Laarbach, *J. prakt. Chem.*, [2] **21**, 159 (1880).

[12] Read, Sharp and Dohme, private communication.

yielded a product which distilled more constantly. Very little of the higher boiling para isomer was obtained. It appears that rearrangement to the para position becomes more difficult the longer the chain.




The odors of thymol, methylthymol and ethylthymol were remarkably similar, the odor sweetening and becoming less phenolic the longer the chain. The odor appears to be characteristic of a tertiary carbon atom ortho to the hydroxyl group in *m*-cresol. These new compounds show extremely high phenol coefficients.

During the course of the research on these and similar compounds it was found that normal propyl, butyl and amyl *p*-cresyl ethers would not rearrange, but gave rise to the original phenol and the corresponding alkyl acetate. All of the secondary alkyl phenyl ethers studied, rearranged, while tertiary alkyl phenyl ethers gave the best yield of substituted phenol on rearrangement. The rearrangement of these ethers is a simple method for preparing the respective substituted alkyl phenols, which would be difficult to prepare otherwise.

The theoretical side of these intramolecular rearrangements may now be examined, but before any reaction mechanism is advanced the following points have to be taken into consideration: (*a*) the reaction appears to be unimolecular in nature; (*b*) the reaction is not reversible; (*c*) rearrangement is possible by the mere application of heat, or (*d*) by the use of a rearranging agent which then seems to play the part of a catalyst.

The phenomena of the rearrangement of unsaturated phenyl ethers (allyl and crotonyl phenyl ethers) have been studied extensively by Claisen and his co-workers,[13] who advanced a reaction mechanism which states that the allyl radical does not attach itself to the cyclic nucleus through the same carbon atom which was bound to the oxygen. Such a postulate does not necessarily apply to the rearrangement of the isopropyl phenyl ethers, but in case of longer chain phenyl ethers further studies may reveal formation of metameric compounds supporting Claisen's theory.

The theory of oxonium compound formation as advanced by Van Alphen[14] cannot be applied without reservation to the cases presented herein, because rearrangement of unsaturated and also of long chain saturated alkyl phenyl ethers is possible by mere application of heat.[15]

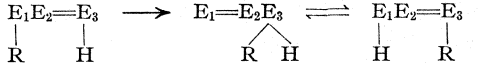
[13] Claisen, *Ann.*, **237**, 261 (1887); **401**, 21, 119 (1914); **418**, 69 (1919); *Ber.*, **58**, 275 (1925); **45**, 3157 (1912); *Z. angew. Chem.*, **36**, 478 (1923); Claisen and Tietze, *Ber.*, **58**, 275 (1925); **59**, 2344 (1926).

[14] Van Alphen, *Rec. trav. chim.*, **46**, 799 (1927).

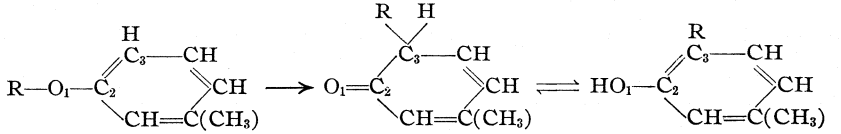
[15] Niederl and Natelson, THIS JOURNAL, **53**, 272 (1931).

The assumption of the formation of free radicals in such intramolecular rearrangements as given by Hurd and Cohen[16] will be somewhat difficult to apply to the above cases, in so far as the simultaneous formation of the possible metameric by-products demanded by rigid application of this theory could not be observed.

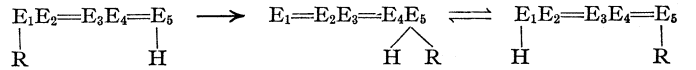
The most plausible explanation for the intramolecular rearrangements presented in this paper appears to be the reaction mechanism advanced by Lapworth[17] for various other types of molecular rearrangements and which is based upon the following arrangement of atomic groupings



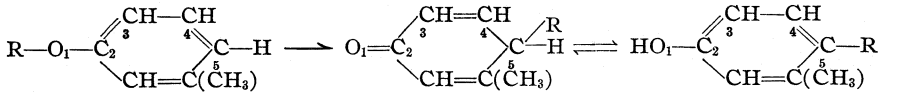
Applied to the cases presented herein the reaction mechanism could then be given for the migration of the alkyl radical to the ortho position



The formation of the para isomer necessitates the following extension of this theory



Applied to the case of the observed formation of the para isomer of thymol (the *m*-methyl-*p*-isopropylphenol) the intramolecular rearrangement can then be illustrated in the following manner



The two phases of the reaction, the disorganization (quinoid form) followed by the reorganization (benzoid form) of the molecule involving tautomeric intramolecular changes can thus be clearly indicated.

The mechanism of these intramolecular rearrangements becomes clearer when the repulsive energies of the atomic kernels in the bonds involved are taken into consideration. In the above reaction the following scheme represents the changes in the bonds during the reaction

$$\underset{\text{Ether}}{(O - C) + (C - H)} \longrightarrow \underset{\text{Phenol}}{(O - H) + (C - C)}$$

According to Latimer,[18] the values of the repulsion energies in the above linkages are

[16] Hurd and Cohen, THIS JOURNAL, **53**, 1917 (1931).

[17] Lapworth, *J. Chem. Soc.*, **73**, 445 (1898).

[18] Latimer, THIS JOURNAL, **51**, 3185 (1929).

$$(O - C) = 2800 \text{ kilocal. repulsion energy}$$
$$(C - H) = 550 \text{ kilocal. repulsion energy}$$
$$(O - H) = 940 \text{ kilocal. repulsion energy}$$
$$(C - C) = 1700 \text{ kilocal. repulsion energy}$$

Substituting these values in the above equation

$$\underset{\text{Ether}}{(2800 + 550)} - \underset{\text{Phenol}}{(940 + 1700)} = 710 \text{ kilocal.}$$

It can then be seen that these intramolecular rearrangements are accompanied by a loss of repulsion energy; the alkyl phenyl ethers with a higher total energy content change into the corresponding substituted phenols with a lower energy potential.

## Experimental Part

**Preparation of the Ethers.**[19]—One molecular weight of *m*-cresol (108 g.), or 4-chloro-*m*-cresol (143 g.) was placed in a three-necked flask fitted with a reflux condenser. Slightly more than one mole of finely divided solid potassium hydroxide was added (60 g.). The whole was gently warmed with a free flame until all the alkali dissolved. Slightly more than one mole of the alkyl halide was added to the mixture drop by drop. The whole was then refluxed for four hours when a light oil separated over precipitated potassium halide. The mixture was allowed to cool and water was added so as to dissolve the potassium halide. The upper layer was separated and washed once with 10% potassium hydroxide and twice with water. The aromatic smelling oil was then dried over calcium chloride and distilled. One distillation was sufficient to obtain a colorless constant boiling liquid.

For commercial preparation of the alkyl cresyl ethers the sulfuric acid,[20] the diazotization,[21] or the condensation method[15] can be made use of and work in this direction is being carried out.

**Rearrangement of the Ethers.**—The rearrangement mixture consists of 200 cc. of concentrated sulfuric acid in sufficient glacial acetic acid to make up to a liter. The following procedure is an improvement on the one reported in a previous article.[9]

One molecular weight of the prepared ether was placed in a round-bottomed flask and 250 cc. of the above mixture added. The mixture was then refluxed for five hours. Two layers separated at first which redissolved to form a homogeneous pink colored solution. The whole was then allowed to cool and poured into an equal volume of saturated salt solution. On long standing, about five hours, a heavy oil separated at the top. This was separated off, washed once with a small quantity of water and then extracted with 600 cc. of 10% potassium hydroxide solution. A small amount of unchanged ether remained which was separated and redistilled to reclaim this starting product. The alkali extract was neutralized with concentrated hydrochloric acid, placing ice in the flask to keep it cool. An oil separated on standing, which was too viscous to handle efficiently and the whole was extracted with ether. The ether was distilled off and the residue fractionated. The colorless oil collected was finally refractionated in vacuum.

**Preparation of the Phenoxyacetic Acid Derivatives.**—Two grams of the substituted phenol was added to one gram of solid potassium hydroxide dissolved in 15 cc. of water. This mixture was warmed on a water-bath until complete solution took place. If an

[19] Williamson, *J. Chem. Soc.*, **4**, 106 (1851).

[20] Ullmann, *Ann.*, **327**, 104 (1903).

[21] Hantzsch and Vock, *Ber.*, **36**, 2062 (1903).

TABLE I

PHYSICAL CONSTANTS AND ANALYSES OF THE COMPOUNDS PREPARED

| Compound | M. p., °C. | B. p., °C. | Sp. gr., (20°) | $n_D^{20}$ | Analyses, % Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|---|
| Isopropyl *m*-tolyl ether | | 195 | 0.931 | 1.4959 | | | | |
| *Sec.*-butyl *m*-tolyl ether[a] | | 212 | .927 | 1.4989 | | | | |
| *Sec.*-amyl *m*-tolyl ether[a] | | 235 | .920 | 1.4999 | | | | |
| Isopropyl 4-chloro-*m*-tolyl ether | | 231 | 1.085 | 1.5230 | | | | |
| Isopropyl-*m*-cresol (from isopropyl *m*-tolyl ether) | | 231–244 | 0.994 | 1.5280 | 80.00 | 79.84 | 9.33 | 9.39 |
| First fraction (thymol) | | 231–235 | | | | | | |
| Acetic acid derivative | 146 | | | | 69.23 | 69.43 | 7.69 | 7.85 |
| Mixed with thymoxyacetic acid | 145 | | | | | | | |
| Second fraction | | 235–237 | | | | | | |
| Acetic acid derivative | 132–137 | | | | | | | |
| Third fraction (3-methyl-4-isopropylphenol) | | 237–244 | | | | | | |
| Acetic acid derivative | 125 | | | | | | | |
| Mixed with 3-methyl-4-isopropylphenoxyacetic acid[b] | 125 | | | | | | | |
| Chlorothymol[c] (from isopropyl 4-chloro-*m*-tolyl ether) | 59–60 | | | | Cl, calcd., 19.27. | | Found, 19.34 | |
| Methylthymol (from *sec.*-butyl *m*-tolyl ether) | | 246–250 | 0.991 | 1.5289 | | | | |
| Methylthymoxyacetic acid | 149 | | | | 70.25 | 69.62 | 8.11 | 7.98 |
| Ethylthymol (from *sec.*-amyl *m*-tolyl ether) | | 143–145 | 0.990 (10 mm.) | 1.5299 | | | | |
| Ethylthymoxyacetic acid | 151–153 | | | | 71.19 | 70.77 | 8.48 | 8.61 |

[a] M. Siegel, Research report, New York University, 1931.

[b] Niederl and Natelson, THIS JOURNAL, **53**, 1928 (1931); Lambling, *Bull. soc. chim.*, [3] **17**, 360 (1897); Spica, *Gazz. chim. ital.*, **10**, 341 (1880).

[c] Bocchi, *ibid.*, **26**, 11, 103 (1896); Peratoner and Condorelli, *ibid.*, **28**, 214 (1898).

emulsion is formed it should be treated with charcoal while hot and filtered. Two grams of bromoacetic acid was dissolved in 10 cc. of water and 2 drops of phenolphthalein added; 10% potassium hydroxide solution was then added until a permanent pink color was obtained. The two solutions were then mixed and gently boiled for ten minutes. A small portion of norite was then added and the boiling continued for one minute. The mixture was filtered through a fluted filter while hot. The filtrate was allowed to cool and neutralized with concentrated hydrochloric acid. An oil separated which solidified on standing. The crystalline product was then recrystallized from water, or a mixture of benzene and ligroin. The colorless crystals were then dried in an air-bath at 110°.

The authors desire to express their appreciation to Professor Wm. C. MacTavish for the facilities placed so generously at their disposal.

## Summary

The intramolecular rearrangement of isopropyl *m*-cresyl ether, under the influence of a mixture of glacial acetic acid and concentrated sulfuric acid, was studied; thymol and *m*-methyl-*p*-isopropylphenol were the products obtained, thus furnishing a new synthesis of thymol.

Methylthymol, ethylthymol and chlorothymol were prepared in a similar manner, by the rearrangement of the corresponding isomeric ethers, illustrating that the rearrangement of secondary alkyl phenyl ethers is a general reaction.

Theories underlying such intramolecular rearrangements were discussed and a reaction mechanism based upon the considerations of Lapworth and Latimer was proposed.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY]

# BETA-ERGOSTENOL

BY MERRILL C. HART AND HAROLD EMERSON

RECEIVED SEPTEMBER 26, 1931 PUBLISHED MARCH 5, 1932

It was first shown by Mauthner[1] that it is possible to isomerize certain members of the sterol group by saturating chloroformic solutions with hydrochloric acid gas. Mauthner thus converted cholestene to pseudocholestene. He also showed that it was probable that cholesterol itself could be isomerized but it remained for Windaus[2] actually to separate and describe allo-cholesterol.

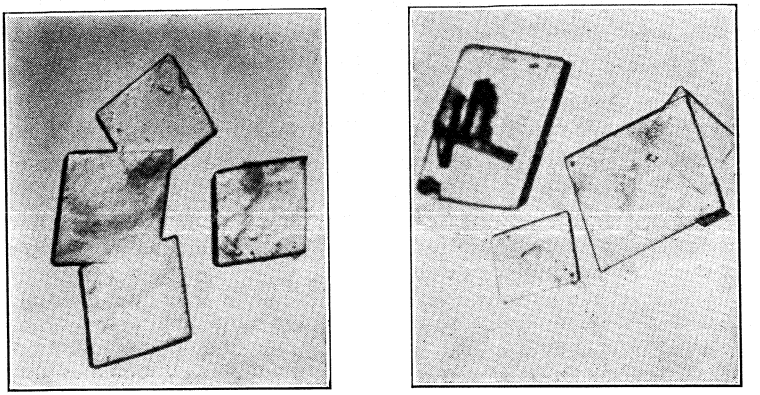
The isomerization of ergosterol by this process was first carried out by Reindel, Walter and Rauch,[3] who also studied this reaction in the case of α-ergostenol. They state that, working with α-ergostenol prepared from

[1] Mauthner, *Monatsh.*, **28,** 1113 (1907).

[2] Windaus, *Ann.*, **453,** 101 (1927).

[3] Reindel, Walter and Rauch, *ibid.*, **452,** 34 (1927); Reindel and Walter, *ibid.*, **460,** 212 (1928).

yeast ergosterol, the reaction yields 95% of the β-isomer. The acetate of β-ergostenol is said to melt at 94–95° and $[\alpha]_D$ +3.0°. This acetate upon saponification gives β-ergostenol melting at 114–118°. The corresponding chloroacetate is said to melt at 166–167°. A complete isomerization of α-ergostenol is said to result upon boiling it with chloroacetyl chloride, for the chloroacetate of β-ergostenol results.



β-Ergostenol acetate. Magnification 7×.

In a previous paper[4] we have indicated our failure to obtain β-ergostenol from the α-form prepared by the reduction of ergosterol from ergot. On every occasion that this reaction was carried out, considerable top fractions of unchanged α-ergostenol acetate could be separated with greatest ease. Furthermore, in preparing the chloroacetate we have shown that the product is largely a chloroacetate of the α-isomer.[5] The esters prepared with monochloroacetyl chloride, trichloroacetyl chloride, propionyl chloride, α-bromopropionyl chloride and butyl chloride, when saponified give obvious mixtures melting at about the same point as that given by Reindel for β-ergostenol.

β-Ergostenol, we believe, has not heretofore been isolated although its existence in the mixture is established by the fact that small amounts of the hexahydroergosterol, allo-α-ergostanol (m. p. 145°) can be prepared by the reduction of the isomerized mixtures, resulting from the above reactions, whereas from α-ergostenol itself no further reduction product can be obtained.

Since the description of the micro method for the determination of hydrogen absorption by Hyde and Scherp,[6] which we have found perfectly adapted to our problem, we have studied the isolation of β-ergostenol from

[4] Hart, Speer and Heyl, THIS JOURNAL, **52,** 2016 (1930).

[5] Hart and Heyl, *ibid.*, **53,** 1413 (1931).

[6] Hyde and Scherp, *ibid.*, **52,** 3359 (1930).

these mixtures, being able to follow the progress of the separation by the determination of the hydrogen absorption of the various fractions. In general the application of Mauthner's process to α-ergostenol yields a mixture containing somewhat less than 50% of the β-isomer, and with considerable difficulty a yield of about 5% can be isolated in pure form.

β-Ergostenol crystallizes from alcohol in plates and melts at 141°, $[\alpha]_D$ +21.2. The details of the properties will be found in the summary.

We consider that β-ergostenol is very probably a good starting point in the study of the degradation of ergosterol. Since α-ergostenol has proved to be such a resistant substance to the ordinary reactions for studying structure, and since, on the contrary, the double bond in the β-isomer is more reactive, it may be hoped to make some progress from β-ergostenol.

## Experimental

**Fractionation of β-Ergostenol.**—α-Ergostenol acetate was isomerized according to the directions of Reindel, Walter and Rauch.[3,7]

The catalytic absorption of hydrogen showed upon analysis that about 45% of the mixture was present as the β-isomer and could be reduced to allo-α-ergostanol. The isomerized mixture of acetates upon one crystallization from ether and alcohol melted at 98–100°.

It was found that the mixture could be more satisfactorily fractionated as the free sterols rather than as the acetates. Twenty-five grams of the mixture of acetates was therefore saponified by boiling with 5% alcoholic potash for thirty minutes. The following successive crops were filtered off.

| Fraction | Weight, g. | M. p., °C. | $H_2$, absorbed, % | Rotation, $[\alpha]_D$ |
|---|---|---|---|---|
| 1 | 4.1 | 100–105 | 35.4 | +14.8 |
| 2 | 7.9 | 110–115 | 41.0 | +16.0 |
| 3 | 5.75 | 120–128 | 65.6 | +21.7 |
| 4 | 0.7 | 90–125 | 56.7 | +29.5 |
| 5 | Sirup, discarded | | | |

These fractions were systematically fractionated from ethyl alcohol. Fraction 1 yielded a considerable quantity of α-ergostenol melting at 133° and forming the characteristic acetate melting at 110°. Fractions 2 and 3 yielded several crops of material of relatively low reducibility which were discarded. Fraction 4 on crystallization from the mother liquors of the above fractions yielded about 3 g. of material crystallizing in flat plates and melting at 133°. Four more crystallizations yielded 1.4 g. that melted at 137°. This material showed on quantitative reduction with hydrogen the presence of 91% of one double bond, $[\alpha]_D$ +23.5°.

This specific rotation (23.5°) is higher than that of the pure β-ergostenol (21.2°). This fact in addition to the fact that fraction 4 has a specific rotation of +29.5° indicates that there is at least one other isomer present, of higher rotation than β-ergostenol. This possibility is being investigated in this Laboratory.

[7] The result of the modification introduced by Windaus, Dithmar, Murke and Suckfüll, *Ann.*, **488**, 91 (1931), of removing the hydrogen chloride from the chloroform solution of the isomerized material before evaporation of the chloroform, is being further studied in the case of ergostenol in this Laboratory as a part of more extended investigation of β-ergostenol and its derivatives.

0.200 g. in 10 cc. of chloroform had a rotation of +0.94° in a 2-dcm. tube at 22°, $[\alpha]_D$ +23.5°. 19.800 mg. in acetic acid absorbed 0.09421 mg. of $H_2$. Calcd. for one double bond in $C_{27}H_{46}O$: $H_2$ required, 0.1033 mg. Found: 0.91 double bond.

**β-Ergostenol Acetate.**—β-Ergostenol was further purified through the acetate. One gram of β-ergostenol (m. p. 137°) was boiled for twenty minutes with an excess of acetic anhydride. The acetate separated in flat plates that melted at 107°. Repeated crystallization from acetic acid raised the melting point to 114°.

*Anal.* Calcd. for $C_{29}H_{48}O_2$: C, 81.2; H, 11.3. Found: C, 81.4; H, 11.1. 0.57 g. in 10 cc. chloroform had a rotation of +1.15° in a 2-dcm. tube at 22°, $[\alpha]_D$ 10.0°. 0.3431 g. was saponified with an excess of alcoholic potash. Calcd. for $C_{29}H_{45}OCOCH_3$: 8.01 cc. of *N*/10 acid. Found: 8.15 cc.

**β-Ergostenol.**—Pure β-ergostenol was prepared by saponification of the acetate and crystallization from alcohol. It separated in plates that melted at 141°.

0.65 g. made up to 10 cc. with chloroform had a rotation of +2.76°, $[\alpha]_D$ 21.2°. 12.882 mg. in acetic acid absorbed 0.0661 mg. of $H_2$. Calcd. for one double bond in $C_{27}H_{46}O$: $H_2$ required, 0.0672 mg. Found: 0.99 double bond.

**Preparation of Allo-α-Ergostanol from Pure β-Ergostenol.**—β-Ergostenol (1.2 g.) was reduced in acetic acid solution with platinum oxide as a catalyst. The reduced material was converted to the acetate and crystallized from acetic acid. Allo-α-ergostanol acetate was obtained in a 72% yield. This crystallized in flat plates that melted at 146° with $[\alpha]_D$ +8.00°.

*Anal.* Calcd. for $C_{29}H_{50}O_2$: C, 80.9; H, 11.7. Found: C, 81.0; H, 11.5. 0.2000 g. was saponified with an excess of alcoholic potash. Calcd. for $C_{27}H_{47}OCOCH_3$: 4.64 cc. of *N*/10 acid. Found: 4.55 cc. 0.200 g. in 10 cc. of chloroform had a rotation of +0.32° in a 2-dcm. tube at 22°, $[\alpha]_D$ +8.00°.

**Allo-α-ergostanol** prepared from the acetate by saponification with alcoholic potash and crystallization from alcohol formed flat hexagonal plates melting at 144° with $[\alpha]_D$ +15.4°.

**Allo-α-Ergostanol Chloroacetate.**—Allo-α-ergostanol (0.100 g.) was gently refluxed for fifteen minutes with an excess of chloroacetyl chloride. After crystallization from acetic acid, 0.067 g. of the chloroacetate melting at 200–201° was obtained.

*Anal.* Calcd. for $C_{29}H_{49}O_2Cl$: Cl, 7.63. Found: Cl, 7.53. 0.050 g. in 10 cc. of chloroform had a rotation of +0.09° in a 2-dcm. tube at 22°, $[\alpha]_D$ +9.0°.

**Ergostenol Chloroacetate Prepared from β-Ergostenol.**—Ergostenol chloroacetate prepared from α-ergostenol and chloroacetyl chloride has been shown[5] to be a mixture of the α- and β-derivatives. Unsuccessful attempts were made to prepare pure β-ergostenol chloroacetate. β-Ergostenol and chloroacetyl chloride yielded a mixture containing equal parts of the α- and β-isomers. The chloroacetate prepared by the use of chloroacetic anhydride was a similar mixture. The results of the action of chloroacetyl chloride and chloroacetic anhydride on α- and β-ergostenol are summarized in Table I.

TABLE I

CHLOROACETATES PREPARED FROM α- AND β-ERGOSTENOL

| Reagent | Chloroacetate M. p., °C. | Chloroacetate Rot. $[\alpha]_D$ | β-form present in reduction, % | Chlorine, % | Hydrolysate M. p., °C. | Hydrolysate Rot. $[\alpha]_D$ |
|---|---|---|---|---|---|---|
| β-Ergostenol + $ClCH_2COCl$ | 168–169 | +8.1 | 50 | 7.75 | 106–112 | +13.8 |
| β-Ergostenol + $(ClCH_2CO)_2O$ | 165–166 | +5.4 | 48 | 7.90 | 115–120 | +16.0 |
| α-Ergostenol + $(ClCH_2CO)_2O$ | 163–166 | +7.8 | 44 | 7.60 | 120–125 | +14.3 |
| α-Ergostenol + $ClCH_2COCl$ | 165–166 | +6.9 | 46 | 7.71 | 110–116 | +14.0 |

## Summary

1. Pure β-ergostenol (m. p. 141°, $[\alpha]_D$ +21.2°) and β-ergostenol acetate (m. p. 114°, $[\alpha]_D$ +10.0°) have been isolated and their properties described.

2. Both chloroacetyl chloride and chloroacetic anhydride reacting on β-ergostenol give a chloroacetyl derivative consisting of a mixture of the α- and β-forms. Approximately this same mixture of α- and β-ergostenol chloroacetates is obtained by the reaction of both chloroacetyl chloride and chloroacetic anhydride on α-ergostenol.

3. α-Ergostenol acetate isomerized by the method of Mauthner consists of a mixture of α- and β-ergostenol acetate with the acetate of at least a third isomer having a higher specific rotation than either α- or β-ergostenol.


KALAMAZOO, MICHIGAN

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY]

# THE STEROLS OF ERGOT. III. THE OCCURRENCE OF AN ISOMER OF ALPHA-DIHYDROERGOSTEROL

BY FREDERICK W. HEYL

RECEIVED SEPTEMBER 26, 1931 PUBLISHED MARCH 5, 1932

Recently[1] we described the isolation of α-dihydroergosterol from the ether–petroleum ether filtrate from crude ergosterol. Not many fractions below the head fraction pure α-dihydroergosterol separated in the process of fractionation with ethyl acetate.

The subsequent fractions show a gradual lowering of the levorotation and from this series there can be repeatedly obtained magnificant plates which greatly resemble the description given for "fungisterol." We are, in fact, convinced that the "fungisterol" of Tanret ($[\alpha]_D$ 15.9°) represents one of these fractions.

From any of these fractions showing $[\alpha]_D$ −6.0° or greater, persistent fractionation, especially of the acetate from a mixture of ether and alcohol, will yield α-dihydroergosterol.

Evidence indicates that the third sterol is optically inactive and that it is practically impossible to separate it in quantity by fractional crystallization of the sterols or of the acetates.

Our purest fraction of the sterol melted at 133–134°. The corresponding acetate, $C_{27}H_{43}OCOCH_3$, melted at 143–145° and had $[\alpha]_D$ −0.5°.

It is unsaturated, giving the Liebermann–Burchard test and quantitatively absorbs two atoms of hydrogen. To color tests it responds exactly as α-dihydroergosterol, with which in fact it appears to be isomeric.

Incidentally the presence of a hydrocarbon, hentriacontane, and of an alcohol, very probably myricyl alcohol, has been observed in the unsaponifiable material from ergot fat.

[1] Heyl and Swoap, THIS JOURNAL, **52**, 3688 (1930).

Neither α-dihydroergosterol nor the new sterol gives an insoluble dibromide, but bromination of the very soluble acetates yielded a minute amount of an insoluble dibromide, m. p. 173–174°. This is evidence of the presence of a fourth sterol. Slight yields of dextrorotatory fractions also indicate the existence of very small quantities of a fourth sterol. We cannot state whether or not the dextrorotatory sterol is the same as the one yielding the insoluble dibromide.

## Experimental

A quantity of crystalline material (386 g.) separating from the petroleum ether filtrates from the preparation of "ergosterol" from ergot was fractionally crystallized from ethyl acetate and separated into thirty-three fractions. Fractions 6, 7 and 8 yielded pure α-dihydroergosterol; and the next seven fractions also yielded the same material but less readily. Fractions 15–22 showed great tendency to separate Tanret's fungisterol.[2]

CRYSTALLIZATIONS FROM FRACTION 23

| | | | Recrystallized | |
|---|---|---|---|---|
| Fraction | Weight, g. | $[\alpha]_D$ | M. p., °C. | $[\alpha]_D$ |
| $V_6$ | 0.6 | −3.9 | 137–141 | −2.8 |
| $V_7$ | .8 | −2.3 | 134–136 | −0.7 |
| $V_8$ | .6 | −4.7 | 133–136 | −1.6 |
| $V_9$ | .8 | −2.2 | 133–134 | −0.0 |
| $V_{10}$ | .2 (discarded) | ... | 124–132 | |

The fractionation resulted in a sharp lowering of the specific rotation between $V_5$ and $V_6$ and this is characteristically obtained in similar fractions. This was accompanied here by the separation of sharply defined sterol crystals having a homogeneous appearance. Upon recrystallization of each of these fractions separately from ether the levorotation is not increased and this is taken as proof of the absence of an excessive quantity of α-dihydroergosterol. If we accept $[\alpha]_D$ −20° for α-dihydroergosterol and assume that the third sterol has no optical activity, then these recrystallized fractions have in no case more than 14% of the predominant sterol. The rotations of the recrystallized fractions are given in the fifth column of the table.

Fractions $V_7$ and $V_9$ recrystallized from ether were selected as the purest material and acetylated. This acetate melted at 141–142°.

Another less pure acetate was prepared as follows. After recrystallizing $V_7$ from ether and obtaining the above described material ($[\alpha]_D$ −0.7°), a second crop was obtained showing ($[\alpha]_D$ −1.1°). In the same way a crop was removed from the ethereal filtrate from $V_9$ recrystallized. It showed ($[\alpha]_D$ −1.5°). These were joined to $V_6$ and $V_8$ recrystallized from ether.

Two fractions of the purest acetate (m. p. 143–145°) upon recrystallization gave $[\alpha]_D$ −0.5° and the subsequent crops from the less pure acetate gave in order −0.6, −1.5, −2.3, −3.3, −4.0, −4.0 and −5.0°.

Since there is no evidence of any dextrorotatory material in this fraction and since the specific rotation of the top fraction continuously approaches zero, we conclude that we have here an almost pure specimen of the third sterol. The acetate was analyzed.

*Anal.* Calcd. for $C_{27}H_{43}OCOCH_3$: C, 81.6; H, 10.87. Found: C, 82.1; H, 10.54.

[2] Tanret gives $[\alpha]_D$ −15.9° in chloroform, *Compt. rend.*, **147**, 75 (1908).

**Color Tests on the New Sterol.**—These resembled those previously given for α-dihydroergosterol. With the Rosenheim trichloroacetic acid reagent, a completely negative test resulted. With the Salkowski test, the chloroform layer was colorless and the sulfuric acid orange-yellow. With the Liebermann–Burchard test the color transitions were as follows: slight pink, transitory lavender, deep blue, slowly changing to green. The Heilbron and Spring modification of the Tortelli–Jaffe reaction was positive.

**Reduction of the New Sterol.**—Quantitative catalytic reductions by the method of Hyde and Scherp[3] showed conclusively the presence of one reducible double bond when using palladium black.[4]

*Anal.* 19.8 mg. of acetate absorbed 0.1166 mg. of $H_2$. Found: 1.2 double bond. 16.83 mg. of acetate absorbed 0.0681 mg. of $H_2$. Found: 0.9 double bond.

0.12 g. of the acetate reduced at room temperature as previously described[5] using, however, palladium black, gave a top fraction (0.07 g.) melting at 103–104°. Upon recrystallization it melted at 110° and a mixed melting point with α-ergostenol acetate was not depressed. Upon saponification with 3% methyl alcoholic potash, α-ergostenol melting at 129–131° was obtained. A mixed melting point with α-ergostenol showed no depression.

**Fraction 24** failed to yield the third sterol of the purity arrived at above due to the appearance in this fraction of a fourth sterol with dextrorotatory properties. A specific rotation of +0.9° was observed in the more soluble part of the series.

**Fraction 25,** obtained by precipitating the ethyl acetate mother liquors with ethyl alcohol, upon repeated crystallization from large volumes of ethyl alcohol, gave a characteristic top fraction melting at 66–75° which was a mixture of myricyl alcohol (m. p. 84–88°) and hentriacontane (m. p. 65–66°).

*Anal.* Calcd. for $C_{31}H_{64}O$: C, 82.2; H, 14.25. Found: C, 82.1; H, 14.0.

*Anal.* Calcd. for $C_{31}H_{64}$: C, 85.3; H, 14.7. Found: C, 84.5; H, 14.6.

The material in the filtrate was acetylated, fractionated and treated with bromine in the usual manner, when a slight yield of a dibromide, crystallizing from alcohol in plates, was obtained (m. p. 173–174°).

*Anal.* Calcd. for $C_{27}H_{43}OCOCH_3Br_2$: Br, 27.25. Found: Br, 25.3.

## Summary

1. The filtrates from α-dihydroergosterol yielded a third ergot sterol $C_{27}H_{43}OH$, melting at 133–134°. This sterol forms an acetate melting at 143–145° and $[\alpha]_D$ −0.5°.

2. The new sterol absorbs two atoms of hydrogen and corresponds to color reactions in the same manner as α-dihydroergosterol.

3. The so-called fungisterol of Tanret is a mixture of α-dihydroergosterol and this new sterol.

4. Myricyl alcohol, $C_{31}H_{64}O$, and hentriacontane, $C_{31}H_{64}$, are shown to be present in ergot fat.

5. The presence of a fourth sterol is definitely indicated by the fact that dextrorotatory fractions were separated from extremely soluble parts of the fractionation. From these an insoluble sterol dibromide was separated.

KALAMAZOO, MICHIGAN

[3] Hyde and Scherp, THIS JOURNAL, **52,** 3359 (1930).

[4] Willstätter and Waldschmidt-Leitz, *Ber.*, **54,** 123, 137 (1921).

[5] Hart, Speer and Heyl, *ibid.*, **52,** 2017 (1930).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY]

# QUANTITATIVE DETERMINATION OF ALPHA-DIHYDROERGOSTEROL IN ERGOSTEROL FROM ERGOT

BY MERRILL C. HART AND HAROLD EMERSON

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Callow[1] has recently showed that ergosterol from yeast contains α-dihydroergosterol. We previously showed this for ergosterol from ergot.[2] In the preceding paper we have found this substance to be the preponderant sterol in the filtrate from ergosterol preparations.

Previously it had been noted in this Laboratory that fine samples of α-ergostenol were regularly prepared from very impure samples of ergosterol. In fact there is no necessity for elaborate purification of ergosterol in proceeding with the preparation of α-ergostenol because, as we know, the impurity α-dihydroergosterol reduces to the same end-product.

In view of the incidental evidence which indicated that the sterols from ergot contained large proportions of α-dihydroergosterol, we have now carefully analyzed a typical ergosterol preparation and find that it contains as much as 30% of α-dihydroergosterol. A third sterol is perhaps present in minute quantity, judging by the slight tendency to impurity of the α-ergosterol prepared from it.

## Experimental

A quantity of "ergosterol" from ergot was prepared in the usual manner[3] and after recrystallization several times from alcohol, melted at 155–157°. The analysis of this material was carried out by first separating 100 g. fractionally into four crystalline crops and a final mother liquor.

We then determined the specific rotation of each fraction. From this value, and the assumption that we are dealing with a mixture of ergosterol for which $[\alpha] = -132°$ and α-dihydroergosterol for which $[\alpha] = -20.4°$, we can calculate the percentage composition.

In order to rule out as far as possible the presence of any appreciable quantity of a third sterol which would render the above calculation somewhat inexact, we reduced two samples of each fraction, in 3-g. quantities, in acetic acid with 0.3 g. of Adams' platinum oxide catalyst in the presence of 2 atmospheres of hydrogen. If the material is simply a mixture of the two sterols as assumed, we would expect a quantitative production of α-ergostenol. The quantitative procedure consisted in concentrating the filtrate from the catalyst to a small volume, saponifying with alcoholic potassium hydroxide, crystallizing from methyl alcohol and quantitatively collecting three successive crops of α-ergostenol. The third crop was separated from small volume. The purity of the α-ergostenol was proved by the melting points and the specific rotation.

Further quantitative recrystallizations of the third fractions enable us to report that the total yield of α-ergostenol in these four fractions is not less than 82, 89, 83 and 85%, respectively.

[1] Callow, *Biochem. J.*, **25**, 87 (1931).

[2] Heyl and Swoap, THIS JOURNAL, **52**, 3688 (1930).

[3] Hart and Heyl, *ibid.*, **52**, 2013 (1930).

TABLE I

RESULTS OF REDUCTION OF ERGOSTEROL FRACTIONS

Ergosterol fractions

| Fraction | M. p., °C. | Weight, g. | Rotation, $[\alpha]_D$ |
|---|---|---|---|
| 1 | 32 | 161 | −123 |
| 2 | 30 | 159 | −110 |
| 3 | 20 | 146–148 | −96.5 |
| 4 | 4[a] | 123–127 | −68 |

Ergostenol fractions

| Frac. | Ergostenol Frac. I Wt., g. | M. p., °C. | Rot., $[\alpha]_D$ | Ergostenol Frac. II Wt., g. | M. p., °C. | Rot., $[\alpha]_D$ | Ergostenol Frac. III Wt., g. | M. p., °C. | Rot., $[\alpha]_D$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3.75 | 133 | +11.1 | 1.2 | 130 | + 9.7 | 0.45 | 110–120 | +4.6 |
| 2 | 3.72 | 133 | +10.4 | 0.8 | 130 | +10.4 | 1.4 | 120–125 | +9.2 |
| 3 | 4.12 | 133 | +10.4 | 0.9 | 129 | + 9.02 | 0.55 | 120–125 | +8.1 |
| 4 | 1.58 | 133 | +10.4 | 1.82 | 132 | + 8.33 | 0.41 | 120–125 | +6.9 |

[a] 4-g. sample used for reduction.

We therefore conclude that from 100 g. of "ergosterol" from ergot, four fractions representing 86% of the original mixture are essentially mixtures of ergosterol and α-dihydroergosterol. We calculate that the top fraction is a mixture of ergosterol 92, α-dihydroergosterol 8%; the second fraction is 80 and 20%; the third is 68 and 32% and the fourth only 42% ergosterol. The total ergosterol from 86 g. is therefore 68.72 g. or about 70% of the total. By difference the α-dihydroergosterol amounts to 30% of the material.

## Summary

"Ergosterol" from ergot consists of a mixture of ergosterol and α-dihydroergosterol, the latter amounting to not less than 30% of the material.

It is shown that the quantitative estimation of this mixture may be carried out polariscopically.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

# FURTHER ATTEMPTS TO SYNTHESIZE SUCROSE

BY JAMES COLQUHOUN IRVINE AND ERIC THOMAS STILLER

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Researches designed to synthesize sucrose by methods consistent with the accepted constitution of the disaccharide had engaged the attention of this Laboratory for some years before Pictet and Vogel[1] announced that they had employed successfully a method which in our hands had failed to give the desired result. The only crystalline gluco-fructose isolated by us was a new isomeric disaccharide which we termed iso-sucrose and regard as β-glucose-β-(γ)-fructoside—nor did we succeed in obtaining evidence that sucrose derivatives were present in the sirupy mixture of condensation compounds from which the octa-acetate of iso-sucrose was separated.

We have not allowed these endeavors to lapse and now submit further results which amplify and confirm our previous findings and lead us to the opinion that the synthesis of sucrose is still an unattained goal. The critical point in such a synthesis lies in the necessity to obtain a tetra-substituted fructose of the γ-type containing in the reducing position a free hydroxyl group through which to couple the corresponding derivative of normal glucose. For many reasons the choice is practically limited to tetra-acetyl-γ-fructose; but this compound is a sirup presenting difficulties in purification and in the proof that during its preparation the internal oxygen linking remains in the same position as in sucrose. In order to meet these difficulties, as described in former papers,[2] we prepared our tetra-acetyl-γ-fructose by different methods and from three different sources, *viz.*, fructose, inulin and sucrose. The products were identical, so far as can be determined with material of this description, and as they were convertible into tetramethyl-γ-fructose there can be no reasonable doubt that the fructose acetate we employed was constituted on the same model as the fructose component of sucrose. We have now prepared tetra-acetyl-γ-fructose by yet another method and in view of the importance of comparing our starting material with that used in other researches with the same objective, the constants of these different specimens of the compound are tabulated below

| Source | A γ-Ethylfructoside (Irvine, Oldham and Skinner) | B Inulin | C Inulin Irvine and Stiller |
|---|---|---|---|
| Refractive index | 1.4645 | 1.4646 | 1.4647 |
| Specific rotation | | | |
| (a) in chloroform | +31.5° | +36.6° | +31.0° |
| (b) in benzene | +38.7° | +41.6° | +35.2° |

[1] Pictet and Vogel, *Helv. Chim. Acta*, **11**, 436 (1928), and subsequent papers.

[2] Irvine, Oldham and Skinner, THIS JOURNAL, **51**, 1279 (1929); Irvine and Oldham, *ibid.*, **51**, 3609 (1929).

| Source | A γ-Ethylfructoside (Irvine, Oldham and Skinner) | B Inulin | C Inulin Irvine and Stiller |
|---|---|---|---|
| Conversion into fructose | | | |
| $[\alpha]_D$ of sugar | −89.8° | −86.3° | −81.7° |
| Percentage yield of fructose as determined by controls | 97.3 | 93.5 | 89.6 |

Process C, as now described, is the speediest and most economical method of preparation but the product possibly contains traces of glucose acetates derived from the inulin, in which case, however, the hexose impurity does not exceed 3%. It may be mentioned also that when titrated with alkali in the cold the liberated acetic acid corresponds to the presence of three in place of four acetyl groups, but this is due to the comparative stability of one acetyl group as the following evidence shows. The compound when methylated by the silver oxide reaction was converted smoothly into tetra-acetyl-γ-methylfructoside containing only one methyl group and giving the correct figures on titration with hot alkali.

The new preparation of tetra-acetyl-γ-fructose, although not entirely homogeneous, shows little variation when fractionated by dissolving in benzene and extracting repeatedly with water.

| | First extract | Final extracts |
|---|---|---|
| Refractive index | 1.4642 | 1.4645 |
| $[\alpha]_D$ in chloroform | +33.9° | +31.5° |
| Acetyl content | 38.5% | 38.6% |

From this evidence we are satisfied that the starting material used in the attempted synthesis now described was actually tetra-acetyl-γ-fructose of not less than 95% purity. A new method was also devised for preparing the tetra-acetylglucose required for the condensations so that we were in a position to use adequate quantities of materials and to vary the conditions of the reaction in several ways.

The method adopted to couple the glucose and fructose residues was essentially the same as before, an equimolecular mixture of the glucose and fructose tetra-acetates being dissolved in a neutral non-hydroxy solvent and shaken with phosphoric anhydride. Variations introduced included (a) the use of either benzene or chloroform as solvent; (b) alterations in the scale of the reaction from the lower limit of 8 g. up to 110 g. of the mixed acetates per experiment; (c) extension of the time of shaking from fifteen hours as a minimum to one hundred and fifteen hours as a maximum; (d) addition of the phosphoric anhydride either in one portion or in several successive installments; (e) the addition of zinc chloride in some experiments and the omission of this reagent in controls.

To economize description the conditions employed in eleven typical condensations are now synopsized in four series.

| | Weight of mixed acetates, g. | Concentration, % | Time of shaking | Additions of $P_2O_5$ |
|---|---|---|---|---|
| | A. Condensations in Benzene without Zinc Chloride | | | |
| I | 20 | 10 | 18 | 1 |
| II | 20 | 10 | 18 | 1 |
| | B. Condensations in Benzene with Zinc Chloride | | | |
| III | 8 | 8 | 22½ | 2 |
| IV | 110 | 10 | 115 | 5 |
| V | 54 | 10 | 115 | 5 |
| VI | 37 | 10 | 115 | 5 |
| | C. Condensations in Chloroform without Zinc Chloride | | | |
| VII | 52.6 | 8 | 17 | 2 |
| VII (a) | 85 | 10 | 15 | 1 |
| | D. Condensations in Chloroform with Zinc Chloride | | | |
| VIII | 88.4 | 8 | 18 | 2 |
| IX | 12.5 | 8 | 15 | 1 |
| X | 12.5 | 8 | 39 | 3 |
| XI | 48 | 8 | 42 | 4 |

The results obtained in the above experiments are now summarized.

SERIES A AND B

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Weight of tetra-acetates used, g. | 20 | 20 | 8 | 110 | 54 | 37 |
| Wt. of tetra-acetates recovered unchanged, g. | 12.2 | 11.9 | 2.1 | 40 | ... | 16 |
| Weight of condensation products, g. | 4.1 | 3.9 | 4.3 | 43.3 | 19 | 13.6 |
| Percentage yield of condensation products | 20.5 | 19.5 | 53.8 | 39.3 | 35.2 | 36.9 |
| Total weight of crystalline products, g. | 0.8 | 0.8 | 1.1 | 3.5 | 3.9[a] | 0.7 |
| Weight of iso-sucrose octa-acetate, g. | .8 | .8 | 1.1 | 3.5 | 0.8 | .7 |

SERIES C AND D

| | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|
| Weight of tetra-acetates used, g. | 52.6 | 88.4 | 12.5 | 12.5 | 48 |
| Wt. of tetra-acetates recovered unchanged, g. | 20.2 | 65.1 | 7.9 | 4.6 | 18 |
| Weight of condensation products, g. | 10.7 | 8.9 | 1.4 | 4.6 | 21 |
| Percentage yield of condensation products | 20.3 | 10.0 | 11.2 | 36.8 | 44 |
| Total weight of crystalline products, g. | 1.8[a] | 0.4[a] | 0.2[a] | 1.4[a] | 3.3[a] |
| Weight of iso-sucrose octa-acetate, g. | 1.2 | Trace | Trace | Trace | 0.9 |

[a] Penta-acetylglucose formed part of the crystalline product.

The irregularity of the results renders generalization impossible but gives an index of the complexity of the reactions involved. The relative yields do not improve with large-scale working but appear to vary in proportion to the time of shaking and with the number of additions of phosphoric anhydride. As a rule, iso-sucrose octa-acetate was the sole crystalline product when the condensations were carried out in benzene solution, but when chloroform was used as solvent, particularly in the presence of zinc chloride, *the iso-sucrose octa-acetate was invariably mixed with glucose penta-acetate.* This significant result, taken in conjunction

with other evidence, gives a clue to some of the secondary reactions involved. Evidently the condensation is accompanied to some extent by the loss of acetyl groups with the consequent formation of acetic anhydride which then effects complete acetylation of the hexoses. As a further complication it may be mentioned that iso-trehalose octa-acetate was present in the crystalline product of Experiment X.

The absence of sucrose derivatives in these solid products made it necessary to focus attention on the non-crystalline condensation compounds. After removal of the unchanged glucose and fructose tetra-acetates from the sirups the acetyl content, with only one exception and that the irregular case of Experiment V, showed that from 30–45% of the material consisted of hexose penta-acetates. Further, polarimetric readings after alkaline hydrolysis followed by acid hydrolysis gave evidence that the glucose and fructose residues participated very unequally in the complex condensations.

NON-CRYSTALLINE CONDENSATION COMPOUNDS

| | I | II | III | VII | VIII | IX | X | XI |
|---|---|---|---|---|---|---|---|---|
| $COCH_3$, % | 59.2 | 56.8 | 60.5 | 60.5 | 59.7 | 52.8 | 60.9 | ... |
| $[\alpha]_D$ after deacetylation | +47.6° | +39.2° | +36.4° | +74.0° | +22.2° | −13.5° | +36.6° | +66.8° |
| $[\alpha]_D$ after hydrolysis | +1.9° | −6.3° | −16.8° | −7.0° | −6.0° | −31.6° | −7.9° | −44.7° |

In each case acid hydrolysis produces a marked fall in dextrorotation amounting generally to an optical inversion, but the irregularity of both the initial and final rotations shows clearly that, in addition to any gluco-fructoses present, some of the mixtures contained excess of di-glucoses and others excess of di-fructoses. Experiment XI is of special interest as the initial rotation is close to that of sucrose but the final value after acid hydrolysis proves that this is adventitious. This result affords a test case, as before hydrolysis all reducing components in the mixture had been removed by heating with dimethylamine and the product re-acetylated.

There remained one final possibility, *viz.*, that the results were complicated by the presence of iso-sucrose octa-acetate in each of the sirupy mixtures, thus obscuring the presence of sucrose octa-acetate and preventing its crystallization. A method was accordingly devised to decompose the less stable iso-sucrose acetate while leaving sucrose derivatives unaffected. Applying this tedious process to the product of Experiment XI as the most promising case, it was found that while the titration value remained unaffected alkaline–acid hydrolysis no longer showed an optical inversion, the change being $[\alpha]_D$ +130.8° ⟶ +35.3°. Other methods of separating any sucrose derivatives which might have been present included the formation and subsequent decomposition of calcium hydroxide compounds, but although the products showed optical inversion during acid

hydrolysis the material could not be induced to crystallize and the initial value was generally much too high in the dextro-sense for sucrose.

In one case only did we succeed in obtaining evidence which might be interpreted as indicating the presence of sucrose in small amount and it is advisable to display the sequence of reactions through which this material passed.

I Condensation of the glucose and fructose acetates.
II Elimination of unchanged glucose and fructose acetates by solution in benzene and extraction with water.
III Removal of iso-sucrose octa-acetate from the condensation products by the action of nitric acid in chloroform solution.
IV De-acetylation and elimination of hexoses (present as penta-acetates) by heating with dimethylamine.
V Formation and decomposition of the calcium hydroxide compounds of any di-saccharides present.

The product was a colorless hard glass which could not be induced to crystallize and failed to give crystalline derivatives. The analytical composition of the acetate agreed approximately with that of sucrose octa-acetate and acid hydrolysis gave the inversion $[\alpha]_D + 71.6° \longrightarrow -13.9°$, figures which are close to those given by sucrose, the divergence being consistent with the presence of traces of di-glucoses. Apart from its failure to crystallize, the material was not entirely homogeneous and its formation represented no more than a 4% yield. As in work of this nature optical compensations are frequently encountered and may easily mislead, we are not inclined to attach importance to the case cited above but think it right to quote it.

## Experimental

As the methods of condensing tetra-acetyl-γ-fructose with tetra-acetyl-glucose and of working up the products have already been detailed in former papers, the following descriptions are limited to new operations; only typical preparations are quoted.

**Tetra-acetyl-γ-fructose.**—Inulin acetate (20 g.) was dissolved in glacial acetic acid (200 cc.) containing 22 cc. of acetyl bromide and the solution preserved in a stoppered bottle until the specific rotation reached a maximum. This value is approximately $[\alpha]_D$ +80° and is attained in about three hours. Thereafter the liquid was transferred to a large beaker, cooled in ice and powdered ice added until the evolution of hydrogen bromide ceased. After the addition of sodium acetate to remove bromine, the solution was diluted largely with water, extracted with chloroform and the extracts dried over sodium sulfate. The chloroform was removed under reduced pressure, the residue dried at 100° and dissolved in benzene, which was extracted with water until the extracts no longer reduced Fehling's solution (15–20 extractions). The combined aqueous layers were then extracted repeatedly with chloroform which was dried and evaporated under reduced pressure. A clear sirup weighing 9.4 g. remained when dried at 100° (10 mm.); yield, 39%.

**Tetra-acetylglucose.**—Penta-acetylglucose (25 g.) was dissolved in 450 cc. of glacial acetic acid to which was added 50 cc. of 40% hydrogen bromide also in acetic

acid solution. In sixty-five minutes the rotation, which increased rapidly, was constant ($[\alpha]_D$ +169°). The solution was poured into 1.5 liters of cold water, 40 g. of sodium acetate added and the liquid heated on a water-bath for two hours at 55°. The product was extracted by chloroform, the extract dried and on removal of the solvent a sirup remained. This was taken up in benzene and the solution extracted with water until all reducing material had been removed. Further treatment of the aqueous extracts was as described above in the case of tetra-acetyl-γ-fructose and an average preparation gives 15–16 g. of analytically pure tetra-acetylglucose in the form of a colorless very viscous sirup; yield, 70%.

**Purification of Non-crystalline Condensation Compounds. A. Removal of Unchanged Hexose Tetra-acetates.**—The total products of each condensation were dissolved in benzene and extracted with water until the extracts were without action upon Fehling's solution. In this way all unchanged tetra-acetates passed into the water while hexose penta-acetates together with disaccharide octa-acetates were retained by the benzene.

**B. Removal of Iso-sucrose Octa-acetate.**—One method, already described and used in some cases in the present research, consists in dissolving the product from A in chloroform containing nitric acid but the following alternative is also satisfactory. A 4% solution of the sirup in glacial acetic acid containing 15% of acetyl bromide was allowed to stand until the specific rotation increased to a constant value. In the case of pure iso-sucrose octa-acetate, complete reaction takes from four to five hours, the optical activity rapidly changing from $[\alpha]_D$ +16.8 to +153.8°; a control carried out on sucrose octa-acetate under duplicate conditions showed no change in rotation for the first three and one-half hours and only a slow elevation thereafter. The reaction should not in consequence be extended beyond four hours.

The solution was poured into ice and water, a slight excess of sodium acetate added and the liquid heated at 50° until the rotation became constant, this treatment being necessary to decompose bromo-sugars. After extracting all products with chloroform, the dissolved sirup was recovered, taken up in benzene and washed repeatedly with water to remove reducing sugars. The benzene solution was finally washed with dilute caustic soda, then with water, dried and evaporated. Two objections apply to this process. Di-glucoses owing to their stability are unaffected and penta-acetylglucose remains unseparated so that the material must subsequently be passed through processes C and D.

**C. Removal of Hexose Penta-acetates.**—Two optional methods were employed, one being the process already described by Irvine, Oldham and Skinner[2] in which the sirup was deacetylated and the liberated hexose destroyed by heating with dimethylamine at 100° for ninety minutes: the disaccharides were thereafter recovered and re-acetylated. The alternative method consisted in dissolving the sirup in glacial acetic acid and saturating with dry hydrogen chloride. After diluting largely with water the liquid was extracted with chloroform, the extracts were dried and evaporated under reduced pressure and the resulting sirup was taken up in benzene. On extracting the solution repeatedly with water, hexose tetra-acetates passed into the aqueous layer and the purified mixture of disaccharide acetates was recovered on evaporating the benzene.

**D. Separation of Disaccharides by Calcium Hydroxide.**—A 10% solution of the sirup in 50% alcohol was heated on a boiling water-bath for one hour with a slight excess of calcium hydroxide prepared directly from calcium. The filtrate was decolorized with norit, taken to dryness in a high vacuum, and extracted with 90% methyl alcohol, the process of evaporation being repeated and absolute methyl alcohol used as the final extracting agent. This treatment removed uncombined disaccharide

together with calcium acetate, the mixture being re-acetylated and the disaccharide octa-acetates separated in the usual way. An amber-colored glass was obtained giving correct analytical figures and showing in a typical case the optical inversion $[\alpha]_D$ $+74.6° \longrightarrow -15.1°$ on alkaline–acid hydrolysis.

As a variation of the above process the initial sirup was de-acetylated with dimethylamine and a 10% aqueous solution boiled for one hour with calcium hydroxide. Carbon dioxide was passed through the hot filtrate for a further hour and the liberated disaccharide isolated as usual. The product was a hard clear glass which despite much endeavor could not be made to crystallize and gave the optical inversion $[\alpha]_D$ $+71.6° \longrightarrow -13.9°$ on acid hydrolysis. These figures resemble closely those given by sucrose but as other disaccharides, including di-glucoses and di-fructoses, would participate equally in all the reactions involved, we regard the resemblance as fortuitous.

The authors gratefully acknowledge their indebtedness to the Carnegie Trust for a Research Scholarship which enabled one of them to undertake this work.

## Summary

1. Additional attempts have been made to synthesize sucrose by the condensation of tetra-acetylglucose with tetra-acetyl-γ-fructose, and new methods have been devised for the preparation of these reagents.

2. Numerous variations have been introduced and the reaction has also been carried out precisely as described by Pictet and Vogel. In no case was sucrose octa-acetate obtained, the only crystalline compounds detected being iso-sucrose octa-acetate, penta-acetylglucose and iso-trehalose octa-acetate either individually or in admixture.

3. The non-crystalline products of the condensation are complex mixtures containing acetylated diglucoses and difructoses, hexose penta-acetates, iso-sucrose octa-acetate and at least one additional gluco-fructose acetate. No evidence was obtained that sucrose octa-acetate was present in these sirups.

4. The iso-sucrose octa-acetate accumulated in the course of the research has been handed to Dr. C. S. Hudson, Washington, D. C., for further examination.

ST. ANDREWS, SCOTLAND

[CONTRIBUTION FROM THE UNIVERSITY OF ST. ANDREWS, SCOTLAND]

# A NEW METHOD OF PREPARING 2-MONOMETHYLGLUCOSE SYNTHESIS OF 2,6-DIMETHYLGLUCOSE

BY JOHN WALTER HYDE OLDHAM AND JEAN KERR RUTHERFORD

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During the course of a recent research conducted in this Laboratory[1] it became necessary to examine the mixture of dimethylglucoses obtained from partially methylated starch by hydrolysis. One of the methods employed consisted in treating the mixed dimethyl methylglucosides with *p*-toluenesulfonyl chloride in order to determine the proportion of sugar unsubstituted in the 6-group. The results obtained are described elsewhere but it may be mentioned here that a crystalline product was isolated which had the composition of a dimethyl methylglucoside di-*p*-toluenesulfonate, and from its small levorotation was evidently the β-form. The compound failed to react with sodium iodide when heated in acetone solution at 100°, showing that group 6 was methylated and, from evidence which has been accumulated in this Laboratory on the chemistry of starch, it was thought most likely that the methyl groups were in positions 2 and 6.

In order to test the correctness of this view it was necessary to compare the above compound with a synthetic specimen of 2,6-dimethyl-3,4-di-*p*-

STAGE A

PREPARATION OF 2-MONOMETHYLGLUCOSE

Glucosemonoacetone ⟶ 3,5,6-Tribenzoylglucosemonoacetone ⟶ 3,5,6-Tribenzoylglucose ⟶ *3,5,6-Tribenzoyl-γ-methylglucoside ⟶ *2-Monomethyl-3,5,6-tribenzoyl-γ-methylglucoside ⟶ *2-Monomethyl-γ-methylglucoside ⟶ 2-Monomethylglucose

STAGE B

CONVERSION INTO THE 2,6-DIMETHYL SERIES

2 Monomethyl glucose

↓

*2-Monomethyl-β-methylglucoside

↓

*2-Monomethyl-3,4,6-tri-*p*-toluenesulfonyl-β-methylglucoside

↓

*6-Iodo-2-methyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside

↓

*2-Monomethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside-6-mononitrate

↓

*2-Monomethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside

↓

*2,6-Dimethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside

* Compounds now described for the first time.

[1] Irvine and Rutherford, forthcoming paper.

toluenesulfonyl-β-methylglucoside. For this purpose the scheme of reactions outlined was selected.

The starting material, *viz.*, 2-monomethylglucose, has until recently been known somewhat vaguely as an uncrystallizable sirup but, after the present work had been begun, Brigl[2] prepared the crystalline sugar from the tetrabenzoate of glucose ethyl mercaptal. Levene, Meyer and Raymond[3] have further examined the compound and identified it with the sugar which was described incorrectly as 4-monomethylglucose by Pacsu.[4] None of the methods hitherto employed for its preparation seem so suitable as the one actually adopted in the present research. The most convenient initial material for the preparation of this substance is the crystalline carbon tetrachloride addition compound of 3,5,6-tribenzoylglucose first described by Fischer[5] and the starting point of the present research was therefore glucosediacetone. Slight modifications were introduced into the preparation of this substance and its conversion into glucosemonoacetone was profoundly modified, the yields being improved to the order of 85% of the theoretical amount. Freudenberg[6] describes an improved method of preparing this substance but he does not state his yields and the length of treatment (four days) is a disadvantage. The removal of the acetone group from tribenzoylglucosemonoacetone was also modified from the method originally described by Fischer. Subsequently the tribenzoylglucose thus obtained was treated with acid methyl alcohol at ordinary temperature until the action on Fehling's solution vanished, the product being thereafter methylated by the silver oxide reaction in the usual manner. The preliminary treatment with acid methyl alcohol appears to be necessary since inferior yields of the methylated sugar are obtained by the direct methylation of tribenzoylglucose. On alkaline saponification followed by acid hydrolysis crystalline 2-monomethylglucose was obtained in good yield. The corresponding β-methylglucoside was in turn converted into the tri-*p*-toluenesulfonyl derivative which, after successive treatment with sodium iodide and silver nitrate followed by removal of the nitrate group and methylation, yielded a crystalline compound, *viz.*, 2,6-dimethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside, identical with that already isolated from the dimethylglucoses obtained from starch. The constitution of 2-monomethylglucose is practically settled by its method of preparation and by its conversion into glucosazone through the loss of a methoxyl group. It was, however, further confirmed by the conversion of the corresponding β-methylglucoside into a benzylidene derivative which

[2] Brigl, *Ber.*, **63**, 1551 and 2884 (1930).
[3] Levene, Meyer and Raymond, *J. Biol. Chem.*, **91**, 497 (1931).
[4] Pacsu, *Ber.*, **58**, 1455 (1925).
[5] Fischer, *ibid.*, **49**, 100 (1916).
[6] Freudenberg, *ibid.*, **61**, 1741 (1928).

on methylation gave the 2,3-dimethyl benzylidene-β-methylglucoside already obtained by Freudenberg[7] from 3-monomethylglucose. It may be mentioned that both 2-monomethylglucose and its benzylidene-β-methylglucoside showed marked depressions of melting point when mixed with 3-monomethylglucose and its benzylidene-β-methylglucoside.

## Experimental

Ninety grams of β-glucose was shaken for sixty hours with 1.5 liters of acetone containing 15–18 g. of hydrogen chloride. The solution was then filtered from unchanged glucose, the amount of which varies greatly, and the filtrate neutralized with excess of a 30–35% solution of sodium hydroxide in the manner described by Minsaas.[8] The upper acetone layer was thereafter decanted, the lower layer washed several times with acetone and the whole taken to dryness at 100° in a flask containing a further small quantity of the soda solution. When all the acetone had been removed, water was added and the aqueous solution extracted three or four times with chloroform. The chloroform extract was shaken with sodium sulfate and charcoal, taken to dryness and dried at 100°. The aqueous layer contained any glucosemonoacetone present, and if this compound be required, the water can be saturated with carbon dioxide, the solution taken to dryness and the dry residue extracted with ethyl acetate. The glucosediacetone obtained from the chloroform is sufficiently pure for conversion into the monoacetone or other easily crystallized derivatives. For conversion to the monoacetone derivative, the diacetone compound was dissolved in 5–8% concentration in 50% aqueous acetone and sufficient aqueous hydrochloric acid added to make the acid concentration in the whole system $N/1000$. The solution was then boiled for thirty to forty-five minutes, the reaction being interrupted as soon as the action on Fehling's solution became at all marked. About three or four times the amount of ammonia solution necessary to neutralize the acid present was then added, and the acetone removed at 100°. The residual aqueous solution was cooled and extracted with chloroform until the extracts were no longer colored. This process removes unaltered glucosediacetone, leaving only glucosemonoacetone, together with any glucose that may have been formed, in the aqueous portion. More ammonia solution was added, the water removed and the well-dried residue repeatedly extracted with ethyl acetate. A typical experiment gave the following yields: 90 g. of β-glucose gave 47 g. of unchanged sugar, and 50 g. of material soluble in chloroform, 8 g. of glucosemonoacetone being recovered from the aqueous layer; 38.8 g. of the material soluble in chloroform gave, after hydrolysis extending for one hour, 5.3 g. of impure glucosediacetone and 6.2 g. of residue insoluble in ethyl acetate. The ethyl acetate extracts gave 18.5 g. of glucosemonoacetone in the first crop and 3 g. in the second. The yield is thus about the theoretical amount if the glucose formed is taken into account. The formation of glucose can be diminished if the time of hydrolysis is shortened but in this case increased quantities of glucosediacetone are recovered unchanged. The material so recovered can be hydrolyzed again but the yields are inferior as they contain all the impurities originally present.

**3,5,6-Tribenzoylglucose.**—Tribenzoylglucosemonoacetone prepared as described by Fischer[5] was boiled for two hours with glacial acetic acid containing 30% of water by volume. After taking to dryness and crystallizing from carbon tetrachloride, in which the addition compound is almost insoluble, 13.1 g. of product was obtained from 16 g. of the starting material, 1.2 g. of unaltered substance being recovered from the mother

[7] Ref. 6, p. 1750.

[8] Minsaas, *Kgl. Norske Videnskab. Selskabs. Forh.*, 1926–1928, I, *Medd.*, No. 2, 113–114 (1929).

liquors. A further small quantity of this material can be obtained if the residue is treated with acid acetone. The yield is thus of the order of 70%.

**2-Monomethyl-3,5,6-tribenzoyl-γ-methylglucoside and 2-Monomethyl-γ-methylglucoside.**—The carbon tetrachloride compound is unsuitable for direct methylation by the silver oxide method as poor yields of final product are obtained. It was therefore first condensed in the cold with 1% acid methyl alcohol until the action on Fehling's solution had completely vanished, and the glucoside isolated by neutralizing with lead carbonate at the boiling point. The product which required no further purification was then methylated two or three times with methyl iodide in the usual manner and the methoxyl content determined. When this approximated to 11.9% the substance was ready for debenzoylation, which was carried out by a method essentially similar to that described by Zemplén.[9] The glucoside was dissolved in methyl alcohol and treated with a small quantity of potassium methylate also dissolved in methyl alcohol, the solution being then boiled for about one minute and a slight deficiency of tartaric acid added after cooling. After adding much water, and filtering if necessary, the solution was extracted with chloroform until the extracts were colorless. A little potassium carbonate solution was then added and the solution taken to dryness at 100°. The well-dried residue was extracted with acetone, filtered and the acetone removed. In this way 2-monomethyl-γ-methylglucoside was obtained as a fairly mobile sirup having $n_D$ 1.4860. No analysis was carried out at this stage. A typical experiment was as follows. The glucoside obtained from 30 g. of the carbon tetrachloride compound was treated with 0.5 g. of potassium methylate followed by 1.5 g. of tartaric acid, 9.4 g. of debenzoylated glucoside being obtained, a yield of 97%, calculating from the carbon tetrachloride compound. This was hydrolyzed with 0.24% aqueous sulfuric acid, the solution being boiled until the rotation became constant, usually after one or two hours. The final specific rotation of the solution varied from +54 to +62°. After neutralizing with barium carbonate the filtrate was taken to dryness at 100°. The crude sugar (yield 94%) crystallized when boiled with absolute alcohol but the yields of crystalline product varied from 58 to 87% of the total product. The reasons for this irregularity are still under investigation. After several recrystallizations from absolute alcohol the sugar, which consists of small prisms, melted after slight sintering at 157–158°. The compound is soluble in water, fairly soluble in methyl alcohol, very slightly so in hot ethyl alcohol, insoluble in other solvents. Calcd. for $C_7H_{14}O_6$: $OCH_3$, 15.9. Found: 16.0. The specific rotation was determined in water and methyl alcohol, in both of which solvents it showed upward mutarotation.

| Time from contact of solvent | Water $c$ = 3.855% | Time from contact of solvent | Methyl alcohol $c$ = 1.88% |
|---|---|---|---|
| 4 minutes | $[\alpha]_D$ + 36.4° | 9 minutes | $[\alpha]_D$ + 25.8° |
| 45 minutes (catalyzed) | + 55.5° | 90 minutes | + 28.0° |
| 15 hours | + 66.0° | 4 hours (catalyzed) | + 32.3° |
| | | 50 hours | + 59.2° |
| | | 74 hours | + 59.7° |

The permanent specific rotations now determined for this sugar in water show good agreement.

| Oldham and Rutherford | Levene and co-workers | Brigl and Schinle |
|---|---|---|
| +66.0° | +62.1° | +65.6° |

The action of acid methyl alcohol in the cold on the sugar was also investigated. For this purpose 15 cc. of the above solution was made up to 20 cc., sufficient hydrogen

[9] Zemplén, *Ber.*, **62**, 1613 (1929).

chloride in methyl alcohol being added to make the total concentration of acid 1%. The reaction was then followed polarimetrically, the following changes being observed

| Time | $[\alpha]_D$ for $c$ = 1.4045% |
|---|---|
| 5 minutes | +66.2° |
| 2.5 hours | +40.5° |
| 6.5 hours | + 9.6° |
| 24.5 hours | −17.9° (The solution no longer reduced |
| 48.5 hours | −15.3° Fehling's solution.) |

On treatment of the sugar with phenylhydrazine acetate in the usual manner for osazone formation, 0.6 g. of the sugar gave 0.4 g. of glucosazone, as shown by absence of methoxyl, by the melting point, and mixed melting point with authentic glucosazone. This result alone is sufficient to prove that the methoxyl group is in position 2 of the glucose chain. The phenylhydrazone of the sugar, previously described by Brigl,[2] was prepared, giving crystals which melted at 176°.

**2-Monomethyl-3,4,6-tri-*p*-toluenesulfonyl-β-methylglucoside.**—2-Monomethylglucose was converted into its β-glucoside by a method which will be described in a forthcoming paper, together with the properties of the glucoside. One and six-tenths grams of crude glucoside was treated with *p*-toluenesulfonyl chloride in the usual manner, giving 3.0 g. of crystalline and 1.5 g. of sirupy product. The yield of crystals was thus about 60% of the theoretical amount but the over-all yield was about 90%. The product crystallized from a mixture of alcohol and glacial acetic acid in fine needles of m. p. 168–169°, with decomposition, after sintering at 167°. It is sparingly soluble or insoluble in most solvents except chloroform and acetone. Calcd. for $C_{29}H_{34}O_{12}S_3$: $OCH_3$, 9.25. Found: $OCH_3$, 9.41. The rotation in chloroform was $[\alpha]_D$ +13.8° for $c$ = 4.110%.

**6-Iodo-2-monomethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside.**—One and three-tenths grams of the crude *p*-toluenesulfonyl derivative was treated with sodium iodide in the usual manner, giving 1.1 g. of product which gave 0.6 g. on recrystallization in the first crop. This consisted of tufts of fine needles melting at 184-185° with much the same solubilities as the last compound. Calcd. for $C_{22}H_{28}O_9S_2I$: $OCH_3$, 9.9; I, 20.2. Found: $OCH_3$, 9.4; I, 20.4. The rotation in chloroform was $[\alpha]_D$ +26.6° for $c$ = 4.300%.

**2-Monomethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside-6-nitrate.**—This derivative was prepared from the above compound in the usual way, 0.429 g. giving 0.25 g. of pure material. Although the yields in this series of compounds are individually poor, they can be greatly improved by using the iodo compound in the form of a sirup. In this way 2.0 g. of the crude tri-*p*-toluenesulfonyl compound gave 1.5 g. of crude crystals which in turn yielded 1.2 g. of pure product. The crude yield was thus almost 90% of the theoretical amount. The product, which had much the same solubilities as the two previous compounds, crystallized from a mixture of alcohol and glacial acetic acid in fine needles melting at 157–158° and having $[\alpha]_D$ in chloroform −3.4° for $c$ = 2.449%. Calcd. for $C_{22}H_{28}O_{12}S_2N$: $OCH_3$, 11.03; N, 2.49. Found: $OCH_3$, 11.0; N, 2.24.

**2-Monomethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside.**—One and two-tenths grams of the nitrate compound was reduced, as described in other papers, giving 1.1 g. of crude product. This crystallized with difficulty from butyl alcohol in short needles, insoluble in water and petroleum ether but soluble in other solvents. It melted after several recrystallizations at 137–140°, attempts to improve this value being unsuccessful. From 1.1 g. a first crop of 0.35 g. was obtained, 0.4 in the second and 0.1 in the third crop. Calcd. for $C_{22}H_{29}O_{10}S_2$: $OCH_3$, 11.99. Found: $OCH_3$, 11.53. The rotation in chloroform was $[\alpha]_D$ −17.8° for $c$ = 3.535.

**2,6-Dimethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside.**—0.647 g. of crude material was methylated twice in the usual manner with silver oxide and methyl iodide, giving 0.666 g. of product. On treatment with absolute alcohol this gave 0.504 g. in the first crop, m. p. 155–157°. A further very small crop was obtained of about 0.02 g. The properties of this substance are described elsewhere.[10]

**2-Monomethylbenzylidene-β-methylglucoside.**—This was made by the method of Freudenberg.[6] The glucoside was dissolved in benzaldehyde (1 in 3) and shaken with half its weight of zinc chloride. As the mixture went solid almost at once it was warmed at 70° for about three hours, but this was probably unnecessary for completion of the reaction. The mixture was thereafter poured into water after being mixed with benzene. At this stage a large amount of crystalline material separated which was filtered off and proved to be the desired compound. The benzene was taken to dryness after separation from the water and the benzaldehyde removed in a vacuum at 100°. The crystalline material weighed 4.7 g. and 4.4 g. was recovered from the benzene. This latter was treated with a mixture of propyl alcohol and petroleum ether, when a further quantity was isolated. On recrystallization from absolute alcohol, 6.1 g. in all was obtained, representing a yield of about 67% of the theoretical amount.

The material when pure consisted of needles melting at 170–171°, a value which was greatly depressed on mixing with the corresponding compound from 3-monomethylglucose. The product was fairly soluble in chloroform and acetone and sparingly soluble or insoluble in other solvents. Calcd. for $C_{15}H_{20}O_6$: $OCH_3$, 20.9. Found: $OCH_3$, 21.3. The rotation in chloroform was $[\alpha]_D$ −69.2° for $c$ = 4.2.

**2,3-Dimethylbenzylidene-β-methylglucoside.**—The benzylidene compound was methylated twice with silver oxide and methyl iodide in the usual manner, when 0.6 g. of starting material gave 0.4 g. of product after crystallization from absolute alcohol. This melted at 132–135°, a value which was unaltered on admixture with an authentic specimen of 2,3-dimethylbenzylidene-β-methylglucoside, thus further proving the constitution of both 2-monomethyl and of 2,3-dimethylglucose.

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## Summary

1. The preparation of glucosemonoacetone has been greatly facilitated.

2. 2-Monomethylglucose has been prepared by an improved method.

3. 2,6-Dimethyl-3,4-di-*p*-toluenesulfonyl-β-methylglucoside has been synthesized and found to be identical with the product (m. p. 155–157°) of the same composition isolated from starch.

4. 2-Monomethylglucose has been converted through its β-methylglucoside into the benzylidene derivative of 2,3-dimethyl-β-methylglucoside, thereby confirming the constitution of the compounds involved.

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[10] Irvine and Rutherford, forthcoming paper.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

# EFFECT OF SUBSTITUENTS IN CERTAIN CONDENSATIONS OF BENZALDEHYDE

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Previous work in this Laboratory[1] has shown that the interaction of bromine and chlorine derivatives of vanillin with amino compounds is not noticeably hindered unless both positions ortho to the aldehyde group are substituted; even then the hindrance is much less than might be expected. For this reason it was desired to test these derivatives in other reactions involving the aldehyde radical. The benzoin condensation and the Claisen reaction suggested themselves.

The discovery of the benzoin condensation is credited to Wöhler and Liebig,[2] who obtained benzoin by treatment of bitter almond oil with potassium hydroxide solution.[3] Subsequent work has shown that certain substituents prevent this condensation from taking place. Thus, *o*- and *p*-nitrobenzaldehydes,[4] salicylaldehyde,[5] 5-bromo- and 5,6-dibromovanillin[6] failed to give the expected benzoins when treated with potassium cyanide in the usual way. One purpose of the present work was to test the effect of substituents indicated in the last two examples by further study of vanillin derivatives. The list of known benzoins is surprisingly small, and it may be supposed that the character of certain substituents in the required starting material is responsible.

Irvine[5] found that salicylaldehyde methyl ether undergoes the benzoin condensation if none of the free salicylaldehyde is present, which suggests that the hydroxide radical may prevent the reaction. This radical as a phenyl substituent causes acidic properties, and since Lachman[7] found

[1] Raiford and others, THIS JOURNAL, **49**, 1077, 1571 (1927); **50**, 2556 (1928); **52**, 4576 (1930).

[2] Wöhler and Liebig, *Ann.*, **3**, 254, 276 (1832).

[3] It has been shown [Stern, *Z. physik. Chem.*, **50**, 513 (1905)] that the benzoin condensation takes place only in the presence of alkali cyanides. But even under these conditions benzoic acid, benzyl alcohol and mandelic acid nitrile are formed in small amounts [Ekecrantz and Ahlqvist, *Centr.*, **79**, 1689 (1908); Lachman, THIS JOURNAL, **46**, 723 (1924)]. The formation of benzoin in Wöhler and Liebig's experiments, in which they isolated also benzoic acid and an "oily body that is no longer bitter almond oil" and which was shown by Cannizzaro [*Ann.*, **88**, 129 (1853)] to be benzyl alcohol, was doubtless due to the presence of hydrocyanic acid in the bitter almond oil used by them.

[4] Homolka, *Ber.*, **17**, 1902 (1884).

[5] Irvine, *J. Chem. Soc.*, **79**, 670 (1901).

[6] Raiford and Hilman, THIS JOURNAL, **49**, 1571 (1927).

[7] Lachman, *ibid.*, **46**, 708 (1924).

that acids prevent the condensation, it was interesting to study the behavior of the alkali salts of such compounds. When the potassium salts of 5-bromovanillin and *p*-hydroxybenzaldehyde, respectively, were subjected to the action of potassium cyanide in the usual way, the starting materials were recovered almost quantitatively, and no benzoin was detected. Vanillin, likewise, does not give a benzoin, but the methyl ether, veratraldehyde (see experimental part), gave a dark-colored oil that was shown to contain a large percentage of starting material, some of the required benzoin,[8] possibly in polymeric form, and a small quantity of 3,4-dimethoxybenzoic acid. The acid was identified by comparison with a sample synthesized in a different way and by a study of its methyl ester. The presence of the benzoin was indicated by the fact that a portion of the product was converted to the corresponding benzil in nearly quantitative yield by oxidation of its alkaline solution.

Halogenated derivatives were next studied. When 3,4-dimethoxy-5-bromobenzaldehyde was subjected to the action of potassium cyanide in the usual way, some starting material, a small quantity of the corresponding dimethoxybromobenzoic acid and a viscous resin-like material were obtained. This resin reduced Fehling's solution and was oxidized to the required benzil, which latter was obtained in crystalline form and identified by study by its hydrazone.[9] The resin must have contained some of the corresponding benzoin, possibly in polymeric form. When the 2-bromo- and 6-bromo-derivatives of 3,4-dimethoxybenzaldehyde were boiled with the cyanide solution, starting material alone was recovered although special search was made for the acid and the benzoin. In the case of the 6-derivative, which was most readily obtained in quantity, attempts to bring about the condensation by variation of the kind and amount of solvent used were unsuccessful. Methyl, ethyl, propyl, isopropyl and *sec.*-amyl alcohols, and pyridine were used as solvents in different experiments, and the time of heating was varied in repetitions of each. Nothing but starting material could be isolated from the reaction mixtures.

These failures, as well as observations made by others, tend to support the view of Staudinger[10] according to which only aldehydes that are

[8] Hörbye [Dissertation, Dresden, 1917, p. 33] found that treatment of ethylvanillin with varying portions of potassium cyanide solution, with and without alcohol, at room temperature and heated on the water-bath, for short and long periods, gave only a trace of benzoin (for which the author offered no experimental identification), a small amount of resin, and some ethylvanillic acid, while the greater portion of the starting material remained unchanged. Likewise, methylvanillin failed to undergo the condensation.

[9] The fact that only one hydrazine residue was introduced, although an excess of reagent was employed, suggests steric hindrance.

[10] Staudinger, *Ber.*, **46**, 3535 (1913).

easily oxidized to the related acids may be expected to undergo the benzoin condensation.[11]

A second purpose in this work was to test these vanillin substitution products toward the Claisen[12] reaction, by which it was hoped to obtain unsymmetrical ketones for use in further study of the rearrangement of the hydrazones of $\alpha,\beta$-unsaturated ketones to pyrazolines.[13] Both mono- and dibenzalacetone derivatives were obtained from 5- and 6-bromovanillin; 5-nitrovanillin gave only a monobenzal derivative. The monovanillal derivatives were obtained by treatment of the required aldehyde with a large excess of acetone with sodium hydroxide as condensing agent; to obtain the di-compounds the calculated amount of acetone was used with concentrated hydrochloric acid as condensing agent.[14]

## Experimental Part

**3,3',4,4'-Tetramethoxybenzil.**—A mixture of the required methylvanillin,[15] 15 cc. of alcohol, 10 cc. of water and 1 g. of potassium cyanide was boiled under reflux for half an hour, and poured into 50 cc. of cold water. The dark-colored oil that separated was removed by extraction with ether, the liquid dried over anhydrous sodium sulfate, the ether distilled and the residue fractionated under partial vacuum. At 160° and 20 mm. about 60% of the material passed over as an oil that solidified on standing. It melted at 42° and did not depress the melting point of methylvanillin. The viscous amber-colored residue solidified upon cooling to a brittle amorphous solid that was not obtained in crystalline form. It reduced Fehling's solution and was probably the required benzoin or a polymer.[16] When a portion of it was allowed to stand exposed to the air for several months it became opaque in appearance and seemed to lose its amorphous character. Crystallization of this product from acetic acid gave small, yellow, closely matted needles, m. p. 219–220°.[17] A second portion was con-

[11] *o*- and *p*-hydroxybenzaldehyde [Dakin, *Am. Chem. J.*, **42**, 478 (1909)], vanillin [Tiemann, *Ber.*, **9**, 415 (1876)] and 5-bromo-vanillin [Brady and Dunn, *J. Chem. Soc.*, **107**, 1859 (1915)] cannot be oxidized to the respective acids by the usual means, and neither of them undergoes the benzoin condensation.

[12] Although Chiozza [*Ann.*, **97**, 350 (1856)] first studied this type of reaction, and Baeyer [*ibid.*, sp. **5**, 82 (1867)] referred to the action of dehydrating agents on a mixture of benzaldehyde and acetone, its development is due to Claisen and co-workers [*Ber.*, **14**, 349, 2468 (1881); *Ann.*, **223**, 138 (1884), and subsequent papers].

[13] Raiford and Davis [THIS JOURNAL, **50**, 156 (1928)] found that in some instances this rearrangement occurs so rapidly that it is impossible to isolate the hydrazone. Subsequent work, soon to be published from this Laboratory, indicates that the direction of the rearrangement is influenced largely by substituents in the phenyl nuclei of the ketones.

[14] Done by a modification of the method used by Glaser and Tramer [*J. prakt. Chem.*, **116**, 331 (1927)]. This paper contains important references to similar work.

[15] Obtained in 89% yield by Perkin and Robinson's [*J. Chem. Soc.*, **91**, 1079 (1907)] method. See, also, modification by Decker and Koch [*Ber.*, **40**, 4794 (1907)].

[16] A product which probably had the composition of this one was obtained by Vanzetti [*Atti accad. Lincei*, **24**, 467 (1915)], who failed to secure a solid product or to note the presence of starting material and 3,4-dimethoxybenzoic acid.

[17] Fritsch [*Ann.*, **329**, 53 (1903)] recorded 219–220° for this benzil obtained by

verted almost quantitatively into the corresponding benzil when air was bubbled for an hour through a boiling alcoholic potash solution of it. The product was identified by analysis and molecular weight determination.[18]

*Anal.* Subs., 0.3230: $CO_2$, 0.7365; $H_2O$, 0.1565. Calcd. for $C_{18}H_{18}O_6$, C, 65.42; H, 5.49. Found, C, 65.00; H, 5.42. 0.0395g. of substance dissolved in 0.8687 g. of camphor, $\Delta$ = 5.8°. Molecular weight = (40,000)(0.0395)/(0.8687)(5.8) = 314. Calcd. for $C_{18}H_{18}O_6$: mol. wt., 330. Found: 314.

The aqueous layer left after extraction of the oil indicated above was warmed to expel ether, acidified and allowed to stand. The solid that separated was readily soluble in alkali solution and reprecipitated by acids. Repeated crystallization from water gave colorless needles, m. p. 180°. A mixture of the product here in question and 3,4-dimethoxybenzoic acid, prepared as directed by Koelle,[19] melted without depression.

**5-Bromo-3,4-dimethoxybenzaldehyde.**—This was made by a variation of Dakin's[20] method. Fifty grams of 5-bromovanillin was dissolved in 300 cc. of methyl alcohol and 13 g. of potassium hydroxide dissolved in the smallest possible quantity of water was added. While the mixture was kept warm on a water-bath, 80 cc. of dimethyl sulfate was added as rapidly as the vigor of the reaction would permit, and the mixture was then evaporated almost to dryness. About 200 cc. of water was next added, the mixture extracted with ether, the extract dried over anhydrous sodium sulfate and the ether distilled off. The residue distilled between 157 and 162° at 5 mm.; yield 95%. The product melted at 59.5°, which is also the melting point of the first portion to solidify from the melted material.[21] The purity of the product here under consideration was checked by a Carius determination of halogen.

*Anal.* Subs., 0.2923: AgBr, 0.2243. Calcd. for $C_9H_9O_3Br$: Br, 32.65. Found: Br, 32.66.

**5,5'-Dibromo-3,3',4,4'-tetramethoxybenzil.**—A mixture of 15 grams of 5-bromo-3,4-dimethoxybenzaldehyde in 100 cc. of alcohol and 2 g. of potassium cyanide in 10 cc. of water was refluxed for five hours, and then poured into five volumes of water. Extraction with ether removed a resinous material that reduced Fehling's solution, and was readily soluble in cold alcohol. The aqueous layer (A) was reserved for further examination. The resin was allowed to stand exposed to the air for several weeks, and the small yellow crystals that had separated were isolated by extracting the remaining resin with cold alcohol, in which the crystals were almost insoluble. Several repetitions of this treatment gave 4.5 g. of material which, after crystallization from

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the action of nitrous acid on tetramethoxyisonitrosodesoxybenzoin in accordance with the method described by Manasse [*Ber.*, **21**, 2176 (1888)].

[18] The method of observing the melting point required in the Rast method [*Ber.*, **55**, 3727 (1922)] was made more convenient and the accuracy of the determination improved by adoption of a suggestion of Dr. E. P. Clark [Bureau of Chemistry and Soils, U. S. Department of Agriculture]. This involved the replacement of the ordinary magnifying lens by a binocular magnifier.

[19] Koelle's [*Ann.*, **159**, 241 (1871)] product melted at 170–171°, and was probably impure.

[20] Dakin, *Am. Chem. J.*, **42**, 494 (1909).

[21] Dakin reported 65–66°. He recorded no analysis for his product, but assumed that its purity was confirmed by the fact that it could be oxidized into the corresponding acid, the melting point of which he did not check, and that the methyl ester of this acid melted at 69–70°, although Zincke and Francke [*Ann.*, **293**, 185 (1896)] found 71–72° for the ester.

acetic acid, was obtained in yellow needles[22] that melted at 209–210°. It did not reduce Fehling's solution. Analysis for bromine and molecular weight determination indicated the benzil.

*Anal.* Subs., 0.2037: AgBr, 0.1585. Calcd. for $C_{18}H_{16}O_6Br_2$: Br, 32.78. Found: Br, 33.11. 0.0277 g. of substance dissolved in 0.4443 g. of camphor, $\Delta = 5.0°$. Molecular weight = (40,000)(0.0277)/(0.4443)(5.0) = 498.7. Calcd. for $C_{18}H_{16}O_6Br_2$: mol. wt., 488. Found: 498.7.

**Mono-*p*-bromophenylhydrazone of 5,5'-Dibromo-3,3',4,4'-tetramethoxybenzil.**—To a glacial acetic acid solution of 2 g. of the required benzil slightly more than two molecular proportions of *p*-bromophenylhydrazine was added, the mixture gently warmed for a few minutes and then allowed to stand for twenty-four hours. Recrystallization of the solid product from acetic acid gave yellow needles; m. p. 155–156°. The yield of purified material was 37%.

*Anal.* Subs., 0.1280: AgBr, 0.1115. Calcd. for $C_{24}H_{21}O_6N_2Br_3$: Br, 36.53. Found: Br, 37.07.

**5-Bromo-3,4-dimethoxybenzoic Acid.**—The aqueous layer (A) left when the ether layer was separated after extraction of the mixture in which an attempt was made to prepare 5,5'-dibromo-3,3',4,4'-tetramethoxybenzoin, was warmed to remove dissolved ether, acidified and allowed to stand. The solid deposited, about 2 g., was recrystallized from water. It was acidic in character, melted at 190°, and was regarded as 5-bromo-3,4-dimethoxybenzoic acid. Zincke and Francke[23] reported 191° for this product, prepared by a different method, but did not determine its bromine content.

*Anal.* Subs., 0.2605: AgBr, 0.1883. Calcd. for $C_9H_9O_4Br$: Br, 30.65. Found: Br, 30.76.

**2-Bromo-3,4-dimethoxybenzaldehyde.**—This was obtained in 74% yield by alkylation of 2-bromovanillin[24] as described above under the 5-bromo compound. After two crystallizations from dilute methyl alcohol it was obtained in colorless needles that melted at 85–85.5°.

*Anal.* Subs., 0.2310: AgBr, 0.1777. Calcd. for $C_9H_9O_3Br$: Br, 32.65. Found: Br, 32.74.

**Di-(5-bromovanillal)-acetone.**—To a suspension of 15 g. of 5-bromovanillin in a mixture of 150 cc. each of glacial acetic and concentrated hydrochloric acid 2.3 cc. of acetone was added, and the mixture allowed to stand with occasional shaking for four weeks.[25] Gentle warming at the time of shaking seemed to aid in dissolving the solid and possibly favored the reaction. When the mixture was poured into a large volume of water a greenish yellow solid was precipitated; yield, 87%. The solid was shaken with dilute sodium hydroxide solution, the mixture filtered and the filtrate acidified with acetic acid. After several repetitions of this treatment the solid was heated with glacial acetic acid until nearly all had dissolved, the mixture filtered, the filtrate poured into several volumes of water, and the precipitate recrystallized from acetic acid. Bright yellow needles that melted at 230–231° were obtained.

*Anal.* Subs., 0.2295: AgBr, 0.1776. Calcd. for $C_{19}H_{16}O_5Br_2$: Br, 33.05. Found: Br, 32.93.

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[22] When the remaining resin from which this benzil had separated was exposed in an open vessel for several months, a nearly colorless sublimate appeared on the walls of the container. This material was identified as 5-bromo-3,4-dimethoxybenzaldehyde.

[23] Zincke and Francke, *Ann.*, **293**, 184 (1896).

[24] Raiford and Stoesser, THIS JOURNAL, **49**, 1077 (1927).

[25] A modification of Glaser and Tramer's [*J. prakt. Chem.*, **116**, 331 (1927)] method.

**6-Bromovanillalacetone.**—Fifteen grams of 6-bromovanillin[26] was dissolved in a mixture of 45 cc. of acetone, 33 cc. of 10% solution of sodium hydroxide and 90 cc. of water[27] and the liquid allowed to stand for several days, during which time a deep red color developed. When the intensity of color increased no further the mixture was poured into several volumes of water, acidified with acetic acid, and the yellow solid collected by filtration; yield, 92%. Two crystallizations from dilute acetic acid gave bright yellow needles; m. p., 153–154°.

*Anal.* Subs., 0.2496: AgBr, 0.1737. Calcd. for $C_{11}H_{11}O_3Br$: Br, 29.52. Found: Br, 29.62.

**Di-(6-bromovanillal)-acetone.**—This was obtained in 75% yield by the above described method for the 5-bromo compound. The product was purified by extraction of foreign material by boiling with glacial acid, in which the desired product was almost insoluble. A bright yellow powder that melted at 255–256° was secured.

*Anal.* Subs., 0.2363: AgBr, 0.1872. Calcd. for $C_{19}H_{16}O_5Br_2$: Br, 33.05. Found: Br, 32.94.

**5-Nitrovanillalacetone.**—Fifteen grams of 5-nitrovanillin[28] was mixed with acetone and dilute alkali solution, allowed to stand for ten days and worked up as specified under the 6-bromo derivative. Crystallization from water gave orange-colored needles; m. p. 156°.

*Anal.* Subs., 0.2171: $CO_2$, 0.4423; $H_2O$, 0.0932. Calcd. for $C_{11}H_{11}O_5N$: C, 55.69; H, 4.63. Found: C, 55.56; H, 4.80.

## Summary and Conclusions

1. Several substituted benzaldehydes have been subjected to the action of potassium cyanide as required in the benzoin condensation. In cases where a bromine atom occupied the ortho position with respect to the aldehyde group, the required benzoin was not obtained.

2. Some confirmation has been found for the theory that the hydroxyl group as a substituent in benzaldehyde prevents the benzoin condensation.

3. Several new substituted benzalacetones have been prepared.

4. Further work is in progress in this Laboratory.

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[26] Raiford and Stoesser, THIS JOURNAL, **49**, 1077 (1927).

[27] Francesconi and Cusmano, *Gazz. chim. ital.*, [II] **38**, 70 (1908).

[28] Prepared as directly by Bentley [*Am. Chem. J.*, **24**, 171 (1900)].

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

# THE NUMBER OF STEREOISOMERIC AND NON-STEREOISOMERIC MONO-SUBSTITUTION PRODUCTS OF THE PARAFFINS

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Having successfully derived formulas of the (finite) recursion type permitting the calculation of the number of structurally isomeric alcohols of the methanol series,[1] as typical structurally isomeric mono-substitution products of the saturated aliphatic hydrocarbons, our attention was directed to an attempt to derive the number of stereoisomeric mono-substitution products. Very naturally, our initial efforts were to derive a relationship between the number of stereoisomers and the total number of asymmetric carbon atoms present among the structural isomers, or to determine the number of structural isomers containing one, two, three, etc., asymmetric carbon atoms per molecule. Solution of the problem by these methods seemed possible for it is now generally accepted that the presence of an asymmetric carbon atom in the molecule of an organic compound causes that substance to exist in two stereoisomeric modifications and if more than one asymmetric carbon atom is present the number of modifications possible may be computed by the expression $2^n$, where $n$ represents the number of asymmetric carbon atoms which are structurally distinct. If the asymmetric carbon atoms simultaneously present in a compound are not structurally distinct, the number of stereoisomers is actually less than that so calculated and hence the above expression requires modification. However, in addition to the problem of determining the numbers of structurally distinct asymmetric carbon atoms, pseudo-asymmetry presents a factor which requires consideration. It was soon found that any method, based upon the above schemes, which might permit the calculation of the number of stereoisomers for low carbon contents would be impossible of application at higher carbon contents. The problem was solved only by taking into account the fact that pseudo-asymmetry is related to structure and upon recognition of a method of forming the structural formulas, of the mono-substitution products, very similar to that previously utilized in calculating the number of structural isomers. This method involves the classification of the mono-substitution products into simple types, for each of which the number of stereoisomers may be computed. The types so chosen are those commonly recognized in derivatives of the paraffins, namely, primary, secondary and tertiary.

**Primary.**—The structural formulas of the primary mono-substitution products of the paraffins, $R-CH_2X$, of $N$ total carbon atom content, may be

[1] Henze and Blair, THIS JOURNAL, **53**, 3042–3046 (1931).

formed from those of $N - 1$ carbon atoms, R–X, by removing the substituted group, X, from each and attaching the resulting alkyl radical, R–, to the $-CH_2X$ group. The number of stereoisomeric primary mono-substitution products that may be formed in this way will thus equal the total number of stereoisomeric mono-substitution products of all types containing $N - 1$ carbon atoms. This fact is readily seen for no additional asymmetric carbon atom has been created, through the addition of the $-CH_2X$ group, nor destroyed, since the substituted group X, which differs from any other group in the molecule, is replaced by $-CH_2X$ which also is different from any other group. For these same reasons the number of non-stereoisomeric primary mono-substitution products will equal the total number of non-stereoisomeric mono-substitution products of all types containing $N - 1$ carbon atoms. Therefore, the number of stereoisomeric and non-stereoisomeric primary mono-substitution products may be calculated by the following formulas[2]

$$Ps_N = As_{N-1} \qquad (I_s)$$
$$Pn_N = An_{N-1} \qquad (I_n)$$

where $Ps_N$ is the number of stereoisomeric primary mono-substitution products of $N$ carbon atoms, $As_{N-1}$ is the total number of stereoisomeric mono-substitution products of all types containing $N - 1$ carbon atoms, $Pn_N$ is the number of non-stereoisomeric primary mono-substitution products of $N$ carbon atoms, and $An_{N-1}$ is the total number of non-stereoisomeric mono-substitution products of all types containing $N - 1$ carbon atoms.

**Secondary.**—The structural formulas of the secondary mono-substitution products of the paraffins, RR′>CHX, of $N$ total carbon atom content, may be formed from those of R–X and R′–X (the carbon content of R– plus R′– always equaling $N - 1$) by removing the X group from each and attaching the resulting alkyl radicals, R– and R′–, to the >CHX group. The total number of isomers that may be formed in this way will be conditioned by the number of possible cases of combining with the >CHX group complementary values of R– and R′–.[3] These possible cases are theoretically of two types: (a), in which the two alkyl radicals, R– and R′–, are of unequal carbon content; and (b), in which these are of equal carbon content. Type (b) is actually impossible with a mono-substitution product of an even number of carbon atoms since in this type $N - 1$ must be divisible by two.

[2] It is to be noted that in using the formulas advanced in this treatment, for the calculation of the number of stereoisomeric and non-stereoisomeric mono-substitution products of any given carbon content, the number of stereoisomers and non-stereoisomers of each lesser carbon content must be known.

[3] The values of R– complementary to R′– satisfy the relationship that the total carbon content of R– plus R′– equal $N - 1$.

**Type (a).**—For each of the individual cases of this type the number of possibilities of combining the stereoisomeric and non-stereoisomeric values of both R– and R′– with the >CHX group may be expressed as follows: $As_i \cdot As_j + As_i \cdot An_j + An_i \cdot As_j + An_i \cdot An_j$ which when simplified yields $T_i \cdot T_j$ where $i$ and $j$ are the carbon contents of R– and R′–, respectively, $T_i = As_i + An_i$, and $T_j = As_j + An_j$. Since in these combinations each value of R– is different from each complementary value of R′–, the carbon atom of the >CHX group will become asymmetric and the number of stereoisomers of each case, for it is thus impossible to form a secondary mono-substitution product of this type which is non-stereoisomeric, will equal $2T_i \cdot T_j$. Hence, the total number of stereoisomeric mono-substitution products of this type will equal

$$2 \Sigma T_i \cdot T_j \qquad (\mathrm{IIa_s})$$

where $i$ and $j$ are integers, distinct, and greater than zero, $i + j = N - 1$, and $i > j$.

The number of $T_i \cdot T_j$ terms included in this summation depends on whether $N$ is even or odd.

Even: if $N$ is even the number of terms of type (a) is $(N - 2)/2$
Odd: if $N$ is odd the number of terms of type (a) is $(N - 3)/2$

**Type (b).**—The isomers of this type, in which the carbon contents of R– and R′– are the same, may be further classified into two groups: (1), in which R– and R′– are absolutely identical from the standpoint of both structural- and stereo-isomerism; and (2), in which R– and R′– are not identical.

**Group (1).**—The combinations of this group may be divided into those in which the identical values[4] are stereoisomeric and those in which the identical values are non-stereoisomeric. When identical stereoisomeric values are combined with the >CHX group, no asymmetric carbon atoms are created and hence the number of stereoisomers thus formed will equal the number of such possible combinations, or $As_i$. When identical non-stereoisomeric values are combined with the >CHX group, no asymmetric carbon atoms are created and since the alkyl radicals themselves contain no asymmetric carbon atoms no stereoisomers will result from such combinations.

**Group (2).**—The number of possibilities of combining non-identical complementary values, both stereoisomeric and non-stereoisomeric, of R– and R′– may be represented by the expression $As_i(As_i - 1)/2 + As_i \cdot An_i + An_i(An_i - 1)/2$. Since the carbon atom of the >CHX group becomes asymmetric with each of these combinations, the number of stereoisomers

[4] Combination of identical values signifies that each individual value, whether stereoisomeric or non-stereoisomeric, is combined through the >CHX group only with itself.

will be double the above expression, or $As_i(As_i - 1) + 2As_i \cdot An_i + An_i \cdot (An_i - 1)$.

A summation of the numbers in group (1) and group (2) of type (b) gives an expression for the total number of stereoisomers of this type, which, when simplified, yields

$$(T_i)^2 - An_i \qquad (IIb_s)$$

where $i$ is an integer greater than zero and $2i = N - 1$.

The number of non-stereoisomers of type (b) will equal $An_i$.

$$An_i \qquad (IIb_n)$$

**Tertiary.**—The structural formulas of the tertiary mono-substitution products of the paraffins, $RR'>C<XR''$, of $N$ total carbon atom content, may be formed from those of R–X, R′–X and R″–X (the carbon content of R– plus R′– plus R″– always equaling $N - 1$) by removing the X group from each and attaching the resulting alkyl radicals R–, R′– and R″– to the $>C<X$ group. The total number of isomers that may be thus formed will be conditioned by the total number of possible cases of combining with the $>C<X$ group complementary values of R–, R′– and R″–.[5] These possible cases are theoretically of two types: (a) in which the three alkyl radicals are of different carbon content; (b) in which two of the alkyl radicals are of the same carbon content and different from that of the third; and (c) in which the three radicals are of equal carbon content. Type (c) is actually possible only when $N - 1$ is divisible by three.

**Type** (a).—For each of the individual cases of this type the number of possibilities of combining the stereoisomeric and non-stereoisomeric values of R–, R′– and R″– with the $>C<X$ group may be expressed as follows: $T_i \cdot T_j \cdot T_k$. Since in this type the values of R–, R′– and R″– are different, the carbon of the $>C<X$ group, to which these radicals are attached, is asymmetric and the number of stereoisomers of each case will equal $2T_i \cdot T_j \cdot T_k$. Hence, the total number of stereoisomeric mono-substitution products of this type will equal

$$2 \Sigma T_i \cdot T_j \cdot T_k \qquad (IIIa_s)$$

where $i$, $j$ and $k$ are integers, distinct, and greater than zero, $i + j + k = N - 1$, and $i > j > k$.

The number of $T_i \cdot T_j \cdot T_k$ terms included in this summation depends on whether $N$ is even or odd.

**Even:** if $N/6$ or $(N - 2)/6$ is an integer, the number of terms of type (a) is $(N - 2)(N - 6)/12$; and if $(N + 2)/6$ is an integer, the number of terms is $(N - 4)^2/12$.

**Odd:** if $(N + 1)/6$ or $(N + 3)/6$ is an integer, the number of terms is $(N - 3)(N - 5)/12$; and if $(N - 1)/6$ is an integer the number of terms is $[(N - 4)^2 + 3]/12$.

[5] The values of R– and R′– complementary to R″– satisfy the relationship that the total carbon content of R– plus R′– plus R″– equal $N - 1$.

**Type (b).**—The isomers of this type, in which the carbon content of R– and R′– are the same and different from that of R″–, may be further classified into two groups: (1), in which R– and R′– are absolutely identical from the standpoint of both structural- and stereo-isomerism; and (2), in which R– and R′– are not identical.

**Group (1).**—The combinations of this group may be divided into those in which the identical values are stereoisomeric and those in which the identical values are non-stereoisomeric. When identical stereoisomeric values for R– and R′– are combined through the ⩾C–X group with the values, both stereoisomeric and non-stereoisomeric, of R″– no asymmetric carbon atoms are created and the number of stereoisomers thus formed will equal the number of such possible combinations or $As_i \cdot T_j$. Similarly, when identical non-stereoisomeric values for R– and R′– are combined through the ⩾C–X group with stereoisomeric values for R″–, no asymmetric carbon atoms are created and the number of stereoisomers will equal $An_i \cdot As_j$. The remaining type of combination theoretically possible is that in which identical non-stereoisomeric values for R– and R′– are combined through the ⩾C–X group with non-stereoisomeric values for R″–. Here, likewise, no asymmetric carbon atoms are created and, since the alkyl radicals contain no asymmetric carbon atoms, no stereoisomers will result.

**Group (2).**—The number of possibilities of combining with the ⩾C–X group non-identical complementary values, both stereoisomeric and non-stereoisomeric, of R–, R′– and R″– may be represented by the expression $[As_i(As_i - 1)/2 + As_i \cdot An_i + An_i(An_i - 1)/2] \cdot T_j$. Since the carbon atom of the ⩾C–X group becomes asymmetric with each of these combinations, the number of stereoisomers for each case will be double the above expression.

A summation of the numbers in group (1) and group (2) of type (b) gives an expression for the total number of stereoisomers of each case, which, when simplified, yields $[(T_i)^2 - An_i]T_j + An_i \cdot As_j$. Hence, the total number of stereoisomeric mono-substitution products of this type will equal

$$\Sigma[[(T_i)^2 - An_i] \cdot T_j + An_i \cdot As_j] \qquad (\text{IIIb}_s)$$

where $i$ and $j$ are integers, distinct, and greater than zero, and $2i + j = N - 1$.

The number of terms of type (b) also depends on whether $N$ is even or odd.

**Even:** if $N/6$ or $(N - 2)/6$ is an integer, the number of terms of type (b) is $(N - 2)/2$; and if $(N + 2)/6$ is an integer, the number of terms is $(N - 4)/2$.

**Odd:** if $(N + 1)/6$ or $(N + 3)/6$ is an integer, the number of terms is $(N - 3)/2$; and if $(N - 1)/6$ is an integer, the number of terms is $(N - 5)/2$.

The number of non-stereoisomers of type (b) will equal

$$An_i \cdot An_j \qquad (IIIb_n)$$

**Type** (c).—The isomers of this type, in which the carbon contents of R–, R′–, and R″– are the same, are also classified into two groups: (1), in which at least two of the three alkyl radicals are absolutely identical from the standpoint of both structural- and stereo-isomerism; and (2), in which no two of the three alkyl radicals are absolutely identical.

**Group** (1).—The combinations of this group may be divided into those in which the identical values are stereoisomeric and those in which the identical values are non-stereoisomeric. When identical stereoisomeric values for R– and R′– are combined through the $\geqslant$C–X group with the values, both stereoisomeric and non-stereoisomeric, of R″–, no asymmetric carbon atoms are created and the number of stereoisomers thus formed will equal the number of such possible combinations or $As_i \cdot T_i$. Similarly, when identical non-stereoisomeric values for R– and R′– are combined through the $\geqslant$C–X group with stereoisomeric values for R″–, no asymmetric carbon atoms are created and the number of stereoisomers will equal $An_i \cdot As_i$. The remaining type of combination theoretically possible is that in which identical non-stereoisomeric values for R– and R′– are combined through the $\geqslant$C–X group with non-stereoisomeric values for R″–. Here, likewise, no asymmetric carbon atoms are created and, since the alkyl radicals contain no asymmetric carbon atoms, no stereoisomers will result.

**Group** (2).—The number of possibilities of combining non-identical complementary values, both stereoisomeric and non-stereoisomeric, of R–, R′–, and R″–, may be represented by the expression $As_i(As_i - 1)(As_i - 2)/6 + An_i \cdot As_i(As_i - 1)/2 + An_i \cdot As_i(An_i - 1)/2 + An_i(An_i - 1)\cdot(An_i - 2)/6$. Since the carbon atom of the $\geqslant$C–X group becomes asymmetric with each of these combinations, the number of stereoisomers will be double the above expression.

A summation of the numbers in group (1) and group (2) of type (c) gives an expression for the total number of stereoisomers, which, when simplified, yields

$$\frac{2\,T_i + (T_i)^3}{3} - (An_i)^2 \qquad (IIIc_s)$$

where $i$ is an integer greater than zero, and $3i = N - 1$.

The number of non-stereoisomers of type (c) will equal

$$(An_i)^2 \qquad (IIIc_n)$$

The actual use of these formulas may be illustrated in the calculation of the number of stereoisomeric and non-stereoisomeric mono-substitution products of the carbon content of thirteen.

**Primary.**—Stereoisomers

$$Ps_{13} = As_{12} = 12{,}648$$

Non-stereoisomers

$$Pn_{13} = An_{12} = 184$$

**Secondary.**—Type (a), number of terms equals $(N - 3)/2 = 5$.

Stereoisomers

$$\begin{aligned} 2{\cdot}T_1{\cdot}T_{11} &= 2{\cdot}1{\cdot}4486 = 8872 \\ 2{\cdot}T_2{\cdot}T_{10} &= 2{\cdot}1{\cdot}1553 = 3106 \\ 2{\cdot}T_3{\cdot}T_9 &= 2{\cdot}2{\cdot}551 = 2204 \\ 2{\cdot}T_4{\cdot}T_8 &= 2{\cdot}5{\cdot}199 = 1990 \\ 2{\cdot}T_5{\cdot}T_7 &= 2{\cdot}11{\cdot}74 = 1628 \end{aligned}$$

Non-stereoisomers.—There can be no non-stereoisomers of this type.

Type (b), since the quotient of $(N - 1)/2$ is an integer, this term is present.

Stereoisomers

$$(T_6)^2 - An_6 = 28^2 - 8 = 776$$

Non-stereoisomers

$$An_6 = 8$$

**Tertiary.**—Type (a), number of terms (for $(N - 1)/6$ = an integer) equals $[(N - 4)^2 + 3]/12 = 7$.

Stereoisomers

$$\begin{aligned} 2{\cdot}T_9{\cdot}T_2{\cdot}T_1 &= 2{\cdot}551{\cdot}1{\cdot}1 = 1102 \\ 2{\cdot}T_8{\cdot}T_3{\cdot}T_1 &= 2{\cdot}199{\cdot}2{\cdot}1 = 796 \\ 2{\cdot}T_7{\cdot}T_4{\cdot}T_1 &= 2{\cdot}74{\cdot}5{\cdot}1 = 740 \\ 2{\cdot}T_7{\cdot}T_3{\cdot}T_2 &= 2{\cdot}74{\cdot}2{\cdot}1 = 296 \\ 2{\cdot}T_6{\cdot}T_5{\cdot}T_1 &= 2{\cdot}28{\cdot}11{\cdot}1 = 616 \\ 2{\cdot}T_6{\cdot}T_4{\cdot}T_2 &= 2{\cdot}28{\cdot}5{\cdot}1 = 280 \\ 2{\cdot}T_5{\cdot}T_4{\cdot}T_3 &= 2{\cdot}11{\cdot}5{\cdot}2 = 220 \end{aligned}$$

Non-stereoisomers.—There can be no non-stereoisomers of this type.

Type (b), number of terms (for $(N - 1)/6$ = an integer) equals $(N - 5)/2 = 4$.

Stereoisomers

$$\begin{aligned} [(T_1)^2 - An_1]T_{10} + An_1{\cdot}As_{10} &= (1^2 - 1){\cdot}1553 + 1{\cdot}1488 = 1488 \\ [(T_2)^2 - An_2]T_8 + An_2{\cdot}As_8 &= (1^2 - 1){\cdot}199 + 1{\cdot}176 = 176 \\ [(T_3)^2 - An_3]T_6 + An_3{\cdot}As_6 &= (2^2 - 2){\cdot}28 + 2{\cdot}20 = 96 \\ [(T_5)^2 - An_5]T_2 + An_5{\cdot}As_2 &= (11^2 - 5){\cdot}1 + 5{\cdot}0 = 116 \end{aligned}$$

Non-stereoisomers

$$\begin{aligned} An_1{\cdot}An_{10} &= 1{\cdot}65 = 65 \\ An_2{\cdot}An_8 &= 1{\cdot}23 = 23 \\ An_3{\cdot}An_6 &= 2{\cdot}8 = 16 \\ An_5{\cdot}An_2 &= 5{\cdot}1 = 5 \end{aligned}$$

Type (c), since the quotient of $(N - 1)/3$ is an integer, this term is present.

Stereoisomers

$$[2 \cdot T_4 + (T_4)^3]/3 - (An_4)^2 = (2 \cdot 5 + 5^3)/3 - 3^2 = 36$$

Non-stereoisomers

$$(An_4)^2 = 3^2 = 9$$

$$As_{13} = Ps_{13} + Ss_{13} + Ts_{13} = 12{,}648 + 18{,}576 + 5{,}962 = 37{,}186$$

$$An_{13} = Pn_{13} + Sn_{13} + Tn_{13} = 184 + 8 + 118 = 310$$

$$T_{13} = As_{13} + An_{13} = 37{,}186 + 310 = 37{,}496$$

The following table indicates the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins as calculated by the use of the recursion formulas.[6]

TABLE I

NUMBER OF STEREOISOMERIC AND NON-STEREOISOMERIC MONO-SUBSTITUTION PRODUCTS OF THE PARAFFINS

| Carbon content | Primary | | Secondary | | Tertiary | | Totals | | |
|---|---|---|---|---|---|---|---|---|---|
| | Stereo-isomers | Non-stereo-isomers | Stereo-isomers | Non-stereo-isomers | Stereo-isomers | Non-stereo-isomers | Stereo-isomers | Non-stereo-isomers | Total isomers |
| 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| 3 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 2 | 2 |
| 4 | 0 | 2 | 2 | 0 | 0 | 1 | 2 | 3 | 5 |
| 5 | 2 | 3 | 4 | 1 | 0 | 1 | 6 | 5 | 11 |
| 6 | 6 | 5 | 14 | 0 | 0 | 3 | 20 | 8 | 28 |
| 7 | 20 | 8 | 34 | 2 | 6 | 4 | 60 | 14 | 74 |
| 8 | 60 | 14 | 98 | 0 | 18 | 9 | 176 | 23 | 199 |
| 9 | 176 | 23 | 270 | 3 | 66 | 13 | 512 | 39 | 551 |
| 10 | 512 | 39 | 768 | 0 | 208 | 26 | 1,488 | 65 | 1,553 |
| 11 | 1,488 | 65 | 2,192 | 5 | 646 | 40 | 4,326 | 110 | 4,436 |
| 12 | 4,326 | 110 | 6,360 | 0 | 1,962 | 74 | 12,648 | 184 | 12,832 |
| 13 | 12,648 | 184 | 18,576 | 8 | 5,962 | 118 | 37,186 | 310 | 37,496 |
| 14 | 37,186 | 310 | 54,780 | 0 | 18,014 | 210 | 109,980 | 520 | 110,500 |
| 15 | 109,980 | 520 | 162,658 | 14 | 54,578 | 342 | 327,216 | 876 | 328,092 |
| 16 | 327,216 | 876 | 486,154 | 0 | 165,650 | 595 | 979,020 | 1,471 | 980,491 |
| 17 | 979,020 | 1,471 | 1,461,174 | 23 | 504,220 | 981 | 2,944,414 | 2,475 | 2,946,889 |
| 18 | 2,944,414 | 2,475 | 4,413,988 | 0 | 1,539,330 | 1,684 | 8,897,732 | 4,159 | 8,901,891 |
| 19 | 8,897,732 | 4,159 | 13,393,816 | 39 | 4,712,742 | 2,798 | 27,004,290 | 6,996 | 27,011,286 |
| 20 | 27,004,290 | 6,996 | 40,807,290 | 0 | 14,475,936 | 4,763 | 82,287,516 | 11,759 | 82,299,275 |

## Summary

1. No direct or simple relationship appears to exist between the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins and their carbon contents.

[6] The structural formulas of the mono-substitution products of the paraffins, inclusive of a carbon content of ten, were written in connection with the derivation of these recursion formulas. The total number of stereoisomers and non-stereoisomers as indicated by inspection of the above-mentioned structural formulas agreed exactly with the numbers obtained by use of the recursion formulas.

2. Formulas of the (finite) recursion type are advanced which permit the calculation from their carbon content of the number of stereoisomeric and non-stereoisomeric primary, secondary and tertiary mono-substitution products of the paraffins. In using these recursion formulas to calculate the total number of such isomers of any given carbon content, the total number of isomers, both stereoisomeric and non-stereoisomeric, of every lesser carbon content must be known.

3. The total number of isomeric mono-substitution products so obtained agrees exactly through those of the decanes with the numbers required by theory as tested by actually writing the structural formulas and counting the number of stereoisomers and non-stereoisomers.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# RESEARCHES ON PYRIMIDINES. CXXV. THE EFFECT OF DILUTE ACIDS AND OF LIGHT ENERGY ON THYMINE GLYCOL. SYNTHESIS OF ACETYLMETHYLDIALURIC ACID

BY TREAT B. JOHNSON OSKAR BAUDISCH AND ALFRED HOFFMANN

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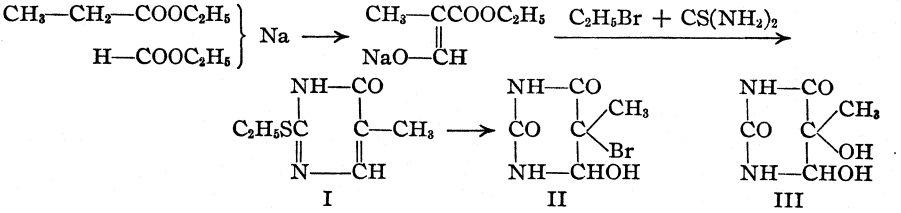
The method of preparing thymine glycol,[1] first described by Baudisch and Davidson, was modified by converting 2-ethylmercapto-5-methyl-6-oxypyrimidine I directly into bromoxyhydrothymine II by the action of bromine and then removing the bromine by the usual procedure to obtain the glycol derivative III. For the preparation of the ethyl mercapto-pyrimidine I the method of Johnson and Schmidt-Nickels[2] was used.




**Method of Preparation.**—Three and one-half grams of 2-ethylmercapto-5-methyl-6-oxypyrimidine I was suspended in 57 cc. of water, and with continuous stirring and gentle warming 5 cc. of bromine was gradually added. A pasty red mass was first formed which, however, on further warming went quickly into solution. The solution, colored with the excess of bromine, was filtered, concentrated *in vacuo*, and the precipitated bromoxyhydrothymine II purified by crystallization from hot water. In later preparations, instead of using silver oxide to replace the bromine in II by hydroxyl as practiced by Baudisch and Davidson, an equivalent amount of silver carbonate was used in order to avoid an alkaline reaction during the change.

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[1] Baudisch and Davidson, *Ber.*, **58**, 1680 (1925).

[2] Johnson and Schmidt-Nickels, THIS JOURNAL, **52**, 4511 (1930).

In the experimental work described below, colorless thymine glycol (III), which is easily soluble in cold water, was used. In previous papers it has been shown that thymine, which is quite stable in alkaline solution and when exposed to light, becomes very sensitive toward alkali through the introduction of the two hydroxyl groups in the pyrimidine ring, and that the previously stable ring is easily broken down even in neutral solution by means of light energy (daylight or carbon arc light). In this change lactic aldehyde is formed as an intermediate decomposition product, which isomerizes into acetol. In weakly alkaline solution thymine glycol breaks down into urea, acetol and carbon dioxide. If at the same time an oxidizing agent is present (atmospheric oxygen in the presence of a catalyst), a different decomposition takes place, leading to the formation of urea, pyruvic acid and carbon dioxide. The biological importance of these characteristic decompositions is quite apparent, and it was especially desirable to learn the effect of dilute mineral acids on thymine glycol in the dark and in the light.

In order to maintain suitable biological conditions throughout our investigations, bacteria which have the power to oxidize sulfur to sulfuric acid were used as the source of acidity. Furthermore, thymine glycol in weak hydrochloric acid solution was irradiated at room temperature with a carbon arc light and the resulting changes studied. In both cases a hitherto unknown anhydride of thymine glycol was formed which is very insoluble in water. In this bacteriological research we were interested above all in a fuchsin-red compound which was formed only in very small quantities and whose chemical constitution we have not yet been able to determine. We will, however, describe carefully its characteristic reactions and especially its behavior to daylight irradiation. It is evident, from our work, that dilute sulfuric acid acts on thymine glycol to form not only the very stable anhydride of thymine glycol, but also a very labile and deeply colored intermediate compound which should be of very great biological interest.

**Effect of Sulfur-oxidizing Bacteria on Thymine Glycol.**—The bacteria used in this research were brought to this country a few years ago by one of the authors (Baudisch) from a Mexican sulfur hot-spring in Santa Rosalia (State of Chihuahua),[3] and were investigated in Waksman's laboratory. From this spring water, or rather from the white sulfur contained therein, a new strain of sulfur-oxidizing bacteria, *Sulphomonas (thiobacillus) thiooxidans*,[4] was isolated. All of the bacteriological research described in this paper was carried out in the Laboratory of Bacteriology at Yale,[5] and

[3] O. Baudisch, "A Mexican Hot Spring," Archives of Medical Hydrology, January, 1929.

[4] See also S. Waksman and Robert L. Starkey, *J. Gen. Physiol.*, No. 3, 285 (1923).

[5] For this privilege we desire to express our appreciation of the courtesy of Professor L. Rettger.

the above-mentioned sulfur bacteria were isolated by Mr. Gibbons from sulfur water shipped recently to us from Santa Rosalia. As a culture medium the pure inorganic salt mixture used by Waksman and Joffe was prepared in the following proportions: 0.2 g. of $(NH_4)_2SO_4$, 0.2 g. of $MgSO_4 \cdot 7H_2O$, 0.25 mg. of $CaCl_2$, 5.0 g. of $KH_2PO_4$ dissolved in 1 liter of distilled water. The cultures were grown in small Erlenmeyer flasks which contained about 50 cc. of culture medium and about 2 g. of flowers of sulfur. The contents of the flasks were sterilized by means of a current of steam and showed a $P_H$ of 4.6, which did not change after standing for several weeks in the incubator. If however the pure inorganic culture medium was inoculated with a loop of *Sulphomonas (Thiobacillus) thiooxidans*, then even after a few days a strong acid formation set in and the hitherto clear contents of the flasks became cloudy, which was a positive indication of an abundant growth of bacteria. If thymine glycol was introduced into the culture medium at the beginning, the growth of the sulfur bacteria proceeded normally, save that the culture medium took on a faint pink color after a few days. Upon further standing in the incubator this color became darker and darker, and after a few weeks the contents of the culture flask were colored a deep fuchsin-red. Without thymine glycol, or after the introduction of thymine, other pyrimidines, sugars, or certain amino acids into the medium, the contents of the culture flask remained colorless in spite of the intensive growth of the bacteria, and in no case except with thymine glycol were pigment formations observed.

A quantitative determination was made of the sulfuric acid formed from the sulfur present in the contents of four flasks, each of which contained 50 cc. of the culture medium and 1 g. of thymine glycol. These flasks had stood for several weeks in the incubator and the contents had become deep red in color. The filtered media of the four flasks were made up to 200 cc. (the original volume) and of this 20 cc. was used for a barium sulfate precipitation. The following results were obtained:

2.2708 g. $BaSO_4$ (from 20 cc. of medium)
$-0.0140$ g. $BaSO_4$ ($SO_4$ ions already in the medium)

2.2568 g. $BaSO_4$ (equivalent of increase in $SO_4$ ions).

From these figures it was calculated that in each flask about 1 g. of sulfur was oxidized to sulfuric acid; the concentration of the sulfuric acid in each flask was about 1 *N*.

In order to determine any change in the thymine glycol during growth, the contents of a flask which had stood for six weeks inthe incubator and which contained 1 g. of this pyrimidine, was filtered from the sulfur and the deep red solution decolorized by exposure to sunlight for a few hours. After evaporation of the clear, colorless solution in a vacuum desiccator, a residue consisting mainly of inorganic salts remained. After trituration with water there remained undissolved a small amount of grayish-white powder which crystallized from boiling water in glistening needles. The weight

was 0.05 g. and the substance melted at 345–350°. The results obtained by analysis indicated that we were dealing here with thymine glycol anhydride.

*Anal.* (Micro) Subs., 3.915, 4.142 mg.: $CO_2$, 6.17, 6.545 mg.; $H_2O$, 1.48, 1.58 mg. Calcd. for $C_5H_6O_3N_2$: C, 42.25; H, 4.23. Found: C, 42.98, 43.09; H, 4.23, 4.27.

When a small amount of the crystals of this anhydride was boiled with *o*-aminobenzaldehyde in alkaline solution, and the solution acidified, *o*-oxyquinaldine was extracted by ether. This experiment proves that when the anhydride of thymine glycol is warmed in alkaline solution, acetol is formed just as in the case of thymine glycol itself, and is easily identified by Baudisch's acetol test. Nothing definite regarding the constitution of this interesting substance has yet been established.

It has previously been mentioned that the deep red sulfuric acid solution of thymine glycol becomes decolorized by exposure to daylight. In order to throw further light on this characteristic photochemical change, pure thymine glycol was dissolved in *N*/5 hydrochloric acid and the solution allowed to stand for a few days in the dark at 37° in an open vessel. The hitherto clear, colorless solution gradually took on a deep red color under the influence of the acid and air. If a part of this red solution was exposed to winter daylight in a glass vessel, it was quickly decolorized, the solution assuming a faint yellow color, and did not become entirely colorless as was the case with the free bacteria experiment. It is easily shown that this decolorization is an oxidation process which is accelerated by light, as dilute hydrogen peroxide decolorizes the solution almost instantaneously. If the deep-red solution is exposed to light in an atmosphere of nitrogen or carbon dioxide, the red color remains unchanged even under intensive irradiation. The weakly yellow solution, decolorized by light from the carbon arc lamp, shows a green fluorescence in ultraviolet light. Upon standing in the incubator in contact with air, the yellow solution quickly regains its red color, although it remains unchanged in a vacuum. Atmospheric oxygen is, therefore, necessary for the formation of the red compound. It is of interest that the long wave ultraviolet rays especially, which are present in sunlight, are strongly absorbed by the red or pale yellow decomposition products of thymine glycol. As an indicator we used crystal violet leucocyanide, a colorless alcoholic solution of which becomes deep blue upon exposure to ultraviolet light. The solution was irradiated in a short glass tube with quartz windows, an iron arc light being used as the light source. If the light is passed through distilled water the leucocyanide becomes noticeably blue in one second. A freshly prepared hydrochloric acid solution of thymine glycol behaves in the same way. However, both the red solution formed on standing in acid solution and the decolorized solution act as strong light filters, and even after irradiation for several minutes the leucocyanide remains colorless. These experiments clearly show that pronounced molecular changes, concerning which we have very little knowledge, take place in the thymine glycol molecule as the result of the influence of acids.

Another indicator useful for the study of these molecular changes was found in color reactions with diazotized sulfanilic acid. Fresh 2% thymine glycol solutions couple with this reagent in alkaline solution, forming a deep red color. This reaction failed, however, if the weakly acid solutions were allowed to stand in atmospheres of nitrogen, carbon dioxide and oxygen, or in a vacuum for several weeks. Through the influence of the acid, changes had taken place in the thymine glycol molecule.

It is striking that the colorless weakly acid thymine glycol solutions remained colorless in nitrogen and carbon dioxide, and assumed only a faint pink color in a vacuum or in oxygen. In contact with the air they became in the same length of time a deep fuchsin red. Similarly the solutions which had been in carbon dioxide and nitrogen atmospheres became red in a few hours when brought in contact with the air. The fuchsin-red solutions first became colorless on making alkaline and then almost

instantaneously a deep yellowish-red due to autoxidation. If first a small amount of cysteine hydrochloride was added to the red solution and the latter then made alkaline, the decolorized solution changed to a deep red from the surface. The red compound formed by the action of acid on thymine glycol is, therefore, colorless in weakly alkaline solution and becomes deep red by autoxidation.

One gram of thymine glycol was dissolved in 100 cc. of *N*/5 hydrochloric acid and the colorless solution placed in the incubator for four weeks, after which time a deep red coloration developed. The flask was then lightly stoppered and kept for two months in a dark room. At the end of this time beautiful ruby-red and also some brown crystals had separated from the remaining 25 cc. of the deep red solution. The aqueous solution was poured off, the crystals thoroughly washed with absolute alcohol, and the ruby red crystals separated from the brown. The melting point of the red crystals was almost the same as that of the thymine glycol used, and the micro-analysis showed the same composition. The brown crystals were soluble in absolute alcohol with the formation of a faint yellow color. When the solution was evaporated to dryness in a vacuum desiccator, a bright yellow residue which could not be crystallized remained. A micro-analysis gave values which agreed well with those of the anhydride of thymine glycol.

In order to determine further the influence of dilute mineral acids on thymine glycol, air was passed through a solution of one gram of thymine glycol in 200 cc. of *N*/5 hydrochloric acid in a quartz cylinder, and the solution irradiated with a strong arc light for several hours under efficient cooling. The solution remained entirely clear and colorless, revealing however an aldehyde-like odor. It was evaporated to dryness in a vacuum desiccator at room temperature. The solid residue was colored a strong pink and was noticeably crystalline. While the original thymine glycol was easily soluble in water, a part of the pink residue remained undissolved. This was filtered off and washed with water, yielding a white powder which crystallized from water in glistening snow-white crystals melting at 340–345°. The weight was 0.25 g.

*Anal.* (Micro) Subs., 4.377 mg.: 0.758 cc. of $N_2$ (26°, 746 mm.). Subs., 4.620 mg. ash-free (0.015 mg. ash), 4.081 mg. (0.012 mg. ash): $H_2O$ 1.77, 1.54 mg.; $CO_2$, 7.19, 6.35 mg. Calcd. for $C_5H_6O_3N_2$: C, 42.25; H, 4.23; N, 19.72. Found: C, 42.44, 42.43; H, 4.29, 4.23; N, 19.41.

Although the new compound is also very insoluble in cold water, it dissolves quickly in alkali and is reprecipitated on acidification. If the alkaline solution is warmed, acetol is split off, which can be identified by Baudisch's acetol reaction.

The filtrate from the crystals above, which had become pink on standing, was again irradiated with cooling. It decolorized rapidly, with the development of an unmistakable aldehyde-like odor. After evaporation in a vacuum desiccator, glistening white crystals, identical with the above-mentioned substance, remained behind and melted at 340–345°.

**The Action of Phosphoric Acid on Thymine Glycol.**—One gram of thymine glycol was dissolved in 50 cc. of commercial phosphoric acid and the clear, colorless solution lightly stoppered and placed in the incubator. Gradually color changes set in and at the end of three months the solution became dark brown and cloudy. It was then diluted with one liter of water, filtered, and the white, insoluble part recrystallized from boiling water, yielding snow-white glistening crystals with a melting point of 345–350°.

*Anal.* (Micro) Subs., 3.915, 4.142 mg.: $H_2O$, 1.48, 1.58 mg.; $CO_2$, 6.17, 6.545 mg. Calcd. for $C_5H_6O_3N_2$: C, 42.25; H, 4.23. Found: C, 42.9, 42.09; H, 4.23, 4.27.

As can be seen from these results, the anhydride of thymine glycol is also formed in phosphoric acid solution, without, however, the formation of the fuchsin-red com-

pound which served as a colorimetric indicator of the acid formation in the sulfur bacterial culture. As has been previously mentioned, the color does not appear in carbon dioxide or nitrogen atmospheres; it is probable that the color is due to the formation of compounds similar in constitution to quinhydrone, which are formed, however, only in the dark and under a certain partial pressure of oxygen. In daylight the fuchsin-red compound quickly takes up more oxygen and is decolorized.

The research below was also carried out in order to clear up further the chemical reactions occurring in an acid thymine glycol solution. The assumption was made from the beginning that at the same time an oxidation process was being dealt with, that the secondary alcohol groups of the thymine glycol molecule were involved first with formation of methyldialuric acid, which has thus far not yet been described in the literature. The preparation and some knowledge of the chemical behavior of this pyrimidine was, therefore, very desirable. We tried to prepare this compound by the direct oxidation of thymine glycol and also by synthesis. Thus far no method which we have applied has given us the desired compound.

## The Oxidation of Thymine Glycol

**Oxidation with Bromine Water.**—Three hundred and twenty milligrams of thymine glycol ($^1/_{500}$ mole) was dissolved in 10 cc. of water and warmed for a short time with 320 mg. of bromine. Neither immediately nor upon standing for fifteen days did the bromine react, as the unchanged color of the solution showed. After evaporation *in vacuo* over sulfuric acid and potassium hydroxide the unchanged thymine glycol was recovered.

**Oxidation with Chromosulfuric Acid.**—Eight hundred milligrams of thymine glycol ($^1/_{200}$ mole) was dissolved in 40 cc. of water, 2 cc. of concd. sulfuric acid added and 5 cc. of 6.6% solution of chromic oxide ($^1/_{200}$ mole of active oxygen). After gentle boiling for about two hours the original red color had changed to green and the mixture gave no test with potassium iodide–starch paper. Barium hydroxide in the calculated amount was added to the gently boiling mixture so that the solution gave a neutral reaction and was free from barium and sulfate ions. After filtering, the filtrate was evaporated to dryness in a vacuum and the residue taken up with a little hot water and filtered. Upon cooling, 153 mg. of a crystalline compound separated out. This was crystallized from 35 parts of water, and separated in the form of interlocking plates. The compound was neutral to litmus, gave no acetol or pyruvic acid test, and did not melt upon heating to 260°, although it sintered at about 175–180°. By means of a green precipitate which it gave with copper ion and by analysis, this substance was recognized as cyanuric acid.

*Anal.* Subs., 101.2 mg.: 27.5 cc. of $N_2$ (22°, 764 mm.). Calcd. for $(CHON)_3$: N, 32.56. Found: N, 32.50.

The formation of the cyanuric acid can be explained by the hydrolysis of thymine glycol by the acid, forming acetol, urea and carbon dioxide. The urea was then oxidized by the chromic acid. In the reaction mixture we were able to identify acetol by means of the Baudisch reaction.

**Oxidation with Red Mercuric Oxide.**—Eight hundred milligrams of thymine glycol ($^1/_{200}$ mole) was dissolved in 500 cc. of water and the solution heated to boiling for a time with a suspension of freshly-prepared mercuric oxide until the oxide dissolved. The solution was then filtered and cooled, when an amorphous, mercury-containing product precipitated, the solution having first become cloudy white. It was impossible to crystallize this substance. For every mole of thymine glycol, one mole of mercury oxide was used, no more going into solution. An analysis of the compound indicates that it has the empirical formula $C_5H_6O_4N_2Hg$.

*Anal.* (Micro) Subs., 118.7 mg.: 8.35 cc. of $N_2$ (22°, 762 mm.). Calcd. for $C_5H_6O_4N_2Hg$: N, 7.83. Found: N, 8.16.

**Synthesis of Acetylmethyldialuric acid.**—(1) An attempt was made to condense chloromethylmalonic acid with urea by means of phosphorus oxychloride according to Grimaux's method. At the end of the experiment a crystalline product separated out which was identified as biuret by means of its crystal structure, reaction, and melting point.

*Anal.* Calcd. for $C_2H_5O_2N_3$: N, 40.78. Found: N, 41.02, 41.1.

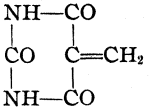
(2) We then attempted to condense ethyl chloromethylmalonate with urea by means of sodium ethylate following the method of Michael: 10.4 g. of chloromethylmalonic ester was mixed with a solution of 1.15 g. of sodium in 25 cc. of absolute alcohol, and the resulting mixture added to a solution of 3 g. of urea in 15 cc. of absolute alcohol. This mixture after heating for seven hours under a reflux condenser gave no condensation product that could be isolated.

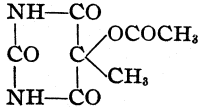
(3) Finally the following method was used. Methylbarbituric acid was prepared and then converted into bromomethylbarbituric acid. After shaking this bromo compound for about twenty hours with silver carbonate, the precipitate was centrifuged off and washed many times with water. After evaporating the solution so made, no residue worth mentioning was obtained. It was then attempted to wash out the centrifugalized residue with hot water, which could not be done however because of the difficulty in filtering. Then the entire precipitate was suspended in water and saturated with hydrogen sulfide. The solution was filtered, evaporated *in vacuo* and the residue redissolved in hot water. On cooling a compound crystallized out in needles which was recrystallized from hot water. It contained sulfur, became yellow at 200–210° and melted with decomposition at about 240–245°. On treatment with alkali no acetol could be identified by the Baudisch test.

*Anal.* (Micro) Subs., 4.401, 4.950 mg.: $H_2O$, 1.08, 1.23 mg.; $CO_2$, 5.625, 6.290 mg. Subs., 4.592 mg.: 0.636 cc. of $N_2$ (26°, 743 mm.). Calcd. for $C_5H_6O_2N_3S$: C, 34.48; H, 3.45; N, 16.08. Calcd. for $C_5H_5O_2N_3S$: C, 34.68; H, 2.89; N, 16.18. Found: C, 34.79, 34.66; H, 2.75, 2.78; N, 15.45.

The results of analysis point to the formation here of a sulfur compound with bimolecular structure and thus far we have come to no definite conclusions regarding its structure.

(4) The following method finally led to the desired result. The bromomethylbarbituric acid was dissolved in 50% acetic acid and a 20% excess of finely pulverized silver acetate added. The mixture was then kept for six hours at 80° with continuous stirring. The silver chloride was filtered off and the excess of silver acetate removed by the careful addition of hydrochloric acid. The solution was then evaporated in a vacuum and the residue taken up in hot water. Upon cooling a crystalline product separated out, which was purified by recrystallization from hot water. It separated as long needles which sintered upon rapid heating to 230°, and decomposed gradually while melting. The properties of this compound and nitrogen determinations indicated that we were not dealing here with a pure substance. The substance reacted as a mixture of the methylene and acetylpyrimidines represented by the formulas





In order to obtain a definite compound from the above reaction product, we then proceeded as follows.

(a) **Acetylation.**—Five hundred milligrams of the above described product was heated for five hours under a reflux condenser with 50 cc. of acetic anhydride which had previously been purified by vacuum distillation. The solvent was removed by vacuum distillation, and the dried residue again taken up in a little acetic anhydride. From the hot filtered solution there separated on cooling 230 mg. of a product which was crystallized in prisms arranged as twins. This melted sharply at 244–245°, solidified again upon cooling, and then melted again about half a degree higher than before.

*Anal.* (Micro) Subs., 107.6, 108.8 mg.: 13.1 cc. of $N_2$ (28°, 763 mm.); 13.0 cc. of $N_2$ (22°, 759 mm.). Calcd. for $C_7H_8O_6N_2$: N, 14.00. Found: N, 13.86, 13.81.

(b) **Saponification.**—Five hundred milligrams of the above described acetyl compound was boiled for five hours under a reflux condenser with 50 cc. of 2 *N* hydrochloric acid, the solvent then distilled off *in vacuo*, the residue taken up in 5 cc. of hot water, and the small amount of the crystalline product which separated on cooling filtered. It was evidently impossible after evaporation in a vacuum desiccator to obtain a crystalline compound. Further work is now in progress, and it is our intention to perfect a practical method of synthesizing this interesting pyrimidine.

## Summary

1. It has been shown previously that thymine glycol is easily broken down in alkaline solution giving urea, acetol and carbon dioxide.

2. In acid solutions the pyrimidine ring of thymine glycol is more stable than in the presence of alkali.

3. Irradiation in acid solution leads to the formation of an anhydride of thymine glycol whose exact constitution is unknown.

4. When thymine glycol is introduced into a culture solution of *Sulphomonas thiooxidans* the latter takes on during incubation a deep red coloration and from the medium the anhydride thymine glycol anhydride can be isolated.

5. Thymine glycol alone in hydrochloric acid solution undergoes the same coloration when allowed to stand in the dark.

6. The red coloration formed in all cases is destroyed by the action of daylight.

7. A method is described for the preparation of acetylmethyldialuric acid.

NEW HAVEN, CONNECTICUT

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

# THE HALOFORM REACTION. V. THE INFLUENCE OF ORTHO BROMINE ATOMS

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The presence in methyl aryl ketones of two ortho methyl groups[1] or two ortho methoxy groups[2] has been found to effect a retardation of the haloform reaction of these ketones such that the trihalomethyl compounds formed as intermediates may be isolated. Although in all of these cases the trihalomethyl ketones have been found to be stable to the action of cold aqueous alkalies, the cleavage has been effected in a number of cases by use of hot concentrated aqueous solutions of alkali. In the case of the methoxy compounds the cleavage is fairly rapid under these conditions but the methyl compounds offer much more resistance to the hydrolytic action of the alkali solutions. The possibility of introducing still larger groups at once suggests itself as a means of studying the effect of hindrance.

Of the ortho disubstituted acetophenones easily obtainable the dibromo would be expected to offer the greatest hindrance and would, therefore, be most suitable for the purpose in view. Actually, 2,4,6-tribromoacetophenone has been found to be the ortho-dibromoacetophenone easiest to prepare and, accordingly, it and its derivatives have been used in this study. In this preparation *m*-nitroacetophenone was used as the starting material. It was reduced by the method of Ullmann and Consonno[3] and the resulting amino compound (I) was brominated by the method of Fuchs.[4] For the removal of the amino group from the tribromo amino ketone (II) the diazotization procedure of Witt[5] using fuming nitric acid and sodium meta-bisulfite was found to be excellent.

2,4,6-Tribromoacetophenone (III) was treated with a solution of sodium hypobromite and after several days was found to have been completely converted into $\alpha,\alpha,\alpha$,2,4,6-hexabromoacetophenone (IV).

The preparation of the corresponding trichloromethyl ketone (V) was, however, much more difficult to accomplish. Long treatment of 2,4,6-tribromoacetophenone with aqueous solutions of sodium hypochlorite caused no change. However, the desired $\alpha,\alpha,\alpha$-trichloro-2,4,6-tribromoacetophenone was eventually obtained by two different methods.

The first method rests upon the plausible but unproved assumption that in the hypohalite halogenations the second and third halogen atoms

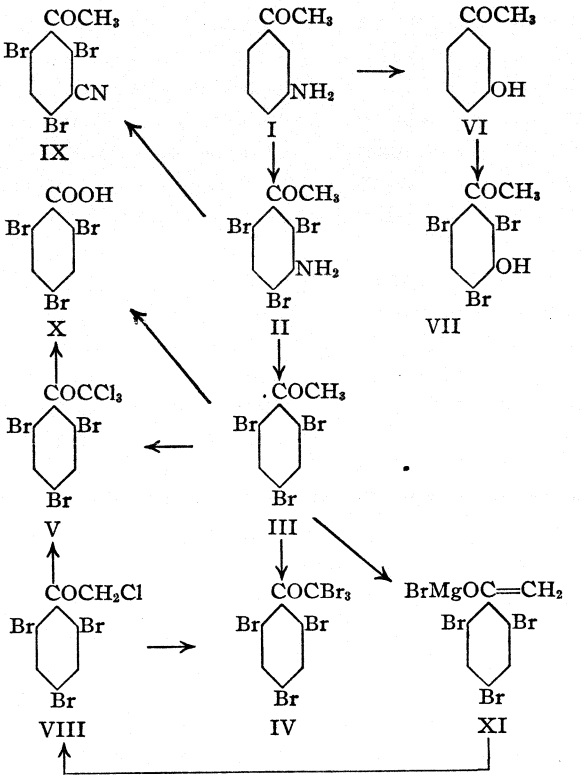
[1] Fuson and Walker, THIS JOURNAL, **52**, 3269 (1930); Gray, Walker and Fuson, *ibid.*, **53**, 3494 (1931).

[2] Fuson, Farlow and Stehman, *ibid.*, **53**, 4097 (1931).

[3] Ullmann and Consonno, *Ber.*, **35**, 2803 (1902).

[4] Fuchs, *Monatsh.*, **36**, 113 (1915).

[5] Witt, *Ber.*, **42**, 2953 (1909).




enter the molecule with greater readiness than does the first. The evidence for this is that in no case of halogenation of methyl ketones by the action of hypohalite solutions has either the mono- or the dihalomethyl derivative been isolated. This would seem to show that halogenation once started proceeds rapidly to completion. In order to test this idea in the present instance 2,4,6-tribromophenacyl chloride (VIII) was prepared and treated with solutions of hypohalites. To prepare the phenacyl chloride 2,4,6-tribromoacetophenone was added to a solution of ethylmagnesium bromide and in this way converted into its bromomagnesium enolate (XI). The enolate was converted into the phenacyl chloride by treatment with chlorine. The results of the halogenation experiments with 2,4,6-tribromophenacyl chloride fully supported the speculations presented above. When treated with solutions of sodium hypochlorite and sodium hypobromite the phenacyl chloride was converted into the $\alpha,\alpha,\alpha$-trichloro-2,4,6-tribromoacetophenone (V) and $\alpha,\alpha,\alpha$,2,4,6-hexabromoacetophenone (IV), respectively.

The second plan for preparing $\alpha,\alpha,\alpha$-trichloro-2,4,6-tribromoacetophenone rests on the idea that the apparent rates of these reactions may be

dependent on solubility factors. Accordingly, pyridine was added to the reaction mixture consisting of 2,4,6-tribromoacetophenone and an aqueous sodium hypochlorite solution. Under these conditions the methyl ketone gave the desired $\alpha,\alpha,\alpha$-trichloro-2,4,6-tribromoacetophenone.

**Cleavage of the Trihalomethyl Ketones by Alkalies.**—Neither the trichloromethyl nor the tribromomethyl ketone could be cleaved by treatment with hot aqueous alkali. However, it seemed likely here also that the rate of reaction might depend on the solubilities of the ketones in water.[6] To test this suggestion methyl alcoholic potassium hydroxide was used. In both cases this treatment produced a reaction but only in the case of $\alpha,\alpha,\alpha$-trichloro-2,4,6-tribromoacetophenone was the expected 2,4,6-tribromobenzoic acid (X) obtained. The tribromomethyl ketone, although it was completely changed, gave neither of the normal cleavage products. However, it was found possible to convert 2,4,6-tribromoacetophenone into 2,4,6-tribromobenzoic acid directly by treatment with aqueous sodium hypobromite in the presence of pyridine and this would seem to indicate the intermediate formation of and subsequent cleavage of $\alpha,\alpha,\alpha$,2,4,6-hexabromoacetophenone.

Another method of getting around the insolubility difficulty in the case of the halogenation was to introduce into the molecule solubilizing groups such as hydroxyl and carboxyl. The first attempt of this sort was to prepare 3-hydroxy-2,4,6-tribromoacetophenone (VII) from *m*-hydroxyacetophenone (VI) by bromination. When this phenolic compound was treated with a hypobromite solution it was slowly transformed into a colorless, alkali-insoluble mass from which no pure compound could be isolated.[7]

In the hope of effecting the desired result in another way the amino group in 3-amino-2,4,6-tribromoacetophenone (II) was replaced by a cyano group to give 3-cyano-2,4,6-tribromoacetophenone (IX) which on hydrolysis should yield the corresponding acid—a compound which would be soluble in alkali. This hydrolysis has as yet not been effected.

## Experimental

**2,4,6-Tribromophenacyl Chloride (VIII).**—To a solution of ethylmagnesium bromide, prepared from 1.5 g. of magnesium and 19 cc. of ethyl bromide, was added

[6] This suggestion is supported by the work of Zincke and his collaborators [Zincke and Günther, *Ann.*, **272**, 250 (1893); Zincke and Francke, *ibid.*, **293**, 147 (1896)], who have prepared alkali-soluble di-ortho substituted trihalomethylacetophenones which were readily cleaved by alkali.

[7] In view of the interesting cleavage results obtained by Lock [*Monatsh.*, **55B**, 307 (1930)] with halogen derivatives of *m*-hydroxybenzaldehyde, it seemed worth while to try the action of concentrated alkali on the tribromo-*m*-hydroxyacetophenone to see if the acetyl group would be removed as is the aldehyde group from the phenolic aldehyde. Although a hot concentrated potassium hydroxide solution was found to change the tribromohydroxy ketone slowly no reaction products could be isolated.

a solution of 17 g. of 2,4,6-tribromoacetophenone dissolved in 100 cc. of anhydrous ether. Heat was evolved during the addition and when all of the ketone had been added a colorless precipitate separated from the solution. After the mixture had been stirred for an hour in an ice–salt bath, the solid was filtered and washed with dry ether. It was then suspended in about 100 cc. of absolute ether and into this mixture chlorine gas was passed for about two hours. The resulting mixture was filtered and the filtrate was evaporated. The residue was pressed on a clay plate to remove oily impurities and then was recrystallized several times from methyl alcohol. The compound melted at 98.0–98.5°; the yield was 7 g. or 38% of the theoretical.

*Anal.*[8] Equivalents of halogen per gram of substance. Calcd. for $C_8H_4OBr_3Cl$: X, 0.0102. Found: X, 0.0101.

**α,α,α,2,4,6-Hexabromoacetophenone (IV). (a) From 2,4,6-Tribromoacetophenone.**—Five grams of tribromoacetophenone was placed in a solution of sodium hypobromite made by dissolving 50 g. of bromine in 500 cc. of 10% aqueous sodium hydroxide at 0°. The mixture was heated over a steam cone in a 500-cc. round-bottomed flask equipped with a mercury-sealed stirrer and a thermometer. The temperature was kept at 40–50° for twenty-four hours, and then at 60–70° for forty hours. The product was washed with water twice, and after crystallization from ethyl alcohol melted at 115–115.5°. The yield was nearly quantitative.

*Anal.* Calcd. for $C_8H_2OBr_6$: Br, 80.8. Found: Br, 80.6.

(b) **From 2,4,6-Tribromophenacyl Chloride (VIII).**—One-half gram of 2,4,6-tribromophenacyl chloride was placed in a flask with 50 cc. of 10% sodium hypobromite solution and stirred for thirteen hours, throughout which time it was heated on a steam-bath. The solid was then filtered and recrystallized from ethyl alcohol. It was shown by the method of mixed melting points to be identical with an authentic specimen of α,α,α,2,4,6-hexabromoacetophenone.

**Attempted Chlorination of 2,4,6-Tribromoacetophenone with Sodium Hypochlorite Solution.**—Two grams of the tribromo ketone was placed in 200 cc. of hypochlorite solution made by passing chlorine gas into 200 cc. of a 10% aqueous sodium hydroxide solution at 0°. The mixture was stirred for three days at room temperature, but no reaction took place. An additional quantity of chlorine was passed into the mixture, which was then allowed to stand at room temperature for four days, but there was still no reaction. Another 2-g. sample was then placed in a flask with 200 cc. of hypochlorite solution, kept at 40° without shaking for two days, and then kept at 50–60° for twelve days. At the end of that time the original substance was recovered unaltered, along with a small amount of silica.

**α,α,α-Trichloro-2,4,6-tribromoacetophenone (V). (a) From 2,4,6-Tribromoacetophenone.**—One-half gram of 2,4,6-tribromoacetophenone was placed in a flask with 10 cc. of pyridine and 30 cc. of a 10% solution of sodium hypochlorite. After being on the shaker for fifteen hours the flask was removed and the small amount of red solid which had separated from the reaction mixture was removed and purified by recrystallization from ligroin. A larger quantity of the product was obtained from the red pyridine layer by acidification and extraction with ether. The product melted at 73–73.5°.

*Anal.* Equivalents of halogen per gram of substance. Calcd. for $C_8H_2OBr_3Cl_3$: X, 0.0130. Found: X, 0.0130.

[8] This and other analyses reported in this paper for compounds containing both chlorine and bromine were carried out by the Parr bomb method in which the total halogen was determined by titration.

(b) **From 2,4,6-Tribromophenacyl Chloride.**—Two grams of 2,4,6-tribromophenacyl chloride was placed in a flask with 200 cc. of a 10% solution of sodium hypochlorite. The mixture was stirred and heated for six days. The solid material was then filtered, pressed on a clay plate to remove some tarry material and crystallized several times from methyl alcohol. The $\alpha,\alpha,\alpha$-trichloro-2,4,6-tribromoacetophenone prepared in this way was shown by the mixed melting point method to be identical with that obtained in (a).

**Reaction of $\alpha,\alpha,\alpha$,2,4,6-Hexabromoacetophenone with Alkali.**—The hexabromoacetophenone was heated for long periods of time with (a) 50% aqueous sodium hydroxide, (b) with methyl alcoholic potassium hydroxide and (c) with a mixture of pyridine and 20% aqueous sodium hydroxide. In all cases the hexabromo compound was decomposed but the only products isolated were tarry substances which could not be purified.

**2,4,6-Tribromobenzoic Acid.** (a) **From 2,4,6-Tribromoacetophenone by Treatment with a Hypochlorite Solution.**—One gram of 2,4,6-tribromoacetophenone was placed in a flask with 25 cc. of pyridine and 25 cc. of a 10% solution of sodium hypochlorite and shaken for four days at room temperature. The red upper layer was then removed and acidified with hydrochloric acid and extracted with ether. The ether was evaporated under diminished pressure and the residue which remained was crystallized from methyl alcohol. The compound melted at 189–190°. The melting point of 2,4,6-tribromobenzoic acid is 188–189°.[9]

(b) **From 2,4,6-Tribromoacetophenone by Treatment with a Hypobromite Solution.**—One gram of 2,4,6-tribromoacetophenone was placed in a flask with 25 cc. of pyridine and 25 cc. of a 10% solution of sodium hypobromite. The mixture was shaken for two days at room temperature and then heated on the steam-bath for two days. It was then acidified and extracted with ether. The ether was evaporated and the 2,4,6-tribromobenzoic acid which was left as a residue was purified by recrystallization from aqueous methyl alcohol. It melted at 189–190° and the melting point showed no lowering when the acid was mixed with a sample of that prepared in (a).

(c) **From $\alpha,\alpha,\alpha$-Trichloro-2,4,6-tribromoacetophenone.**—Two-tenths gram of the trichloromethyl ketone was placed in a test-tube with 15 cc. of a solution of 30% potassium hydroxide in 30% aqueous methyl alcohol. The solution was refluxed in the steam-bath for one day, removed and acidified. After standing for several days the solution deposited a small amount of material melting at 184–186° which was shown to be impure 2,4,6-tribromobenzoic acid.

***m*-Hydroxyacetophenone (VI).**—Fourteen grams of *m*-aminoacetophenone was dissolved in 140 cc. of water and 18 cc. of concentrated sulfuric acid in an 800-cc. beaker. The solution was stirred and cooled in an ice–salt bath, and the amine was diazotized by adding a concentrated solution of 7.2 g. of sodium nitrite. After the addition the solution was boiled until all the nitrogen was driven off. It was then cooled, and the crystals and dark material which separated were boiled with 800 cc. of norite and filtered. The product crystallized after two to three hours in a colorless fluffy mass. The yield of *m*-hydroxyacetophenone was 11 g. or 78.5% of the theoretical. The melting point was 94–94.5°.[10]

**2,4,6-Tribromo-3-hydroxyacetophenone (VII).**—Three grams of pure *m*-hydroxyacetophenone was placed in an 800-cc. beaker with 250 cc. of water. The solution was stirred and heated to 50°, at which temperature bromine was added (about 4 cc.) very slowly until a yellow color persisted in the solution. The product separated as a light tan precipitate. This was washed with dilute sodium bisulfite solution and with

[9] Wegscheider, *Monatsh.*, **18**, 217 (1897).

[10] Rupe and Majewski [*Ber.*, **33**, 3407 (1900)] give the melting point as 95°.

water, and after numerous crystallizations from aqueous methyl alcohol melted at 127.5°.

*Anal.* Calcd. for $C_8H_5O_2Br_3$: Br, 64.3. Found: Br, 64.5.

**Decomposition of 2,4,6-Tribromo-3-hydroxyacetophenone (VII) with Alkali.**—Two grams of 2,4,6-tribromo-3-hydroxyacetophenone was placed in a small Erlenmeyer flask, and to it was added 8 cc. of a 50% potassium hydroxide solution. The mixture was heated on a steam-bath for three days. A small sample was then removed and reprecipitated from dilute acid, but the starting material was obtained. The mixture was then refluxed over a small flame for two days, and a small sample removed and reprecipitated as above. From this material was obtained only a colorless solid which was insoluble in ether, alcohol and acetic acid, but which crystallized from benzene. The melting point of this material was above 400°.

***m*-Cyano-2,4,6-tribromoacetophenone (IX).**—Seven grams of *m*-amino-2,4,6-tribromoacetophenone was diazotized with 6.0 cc. of concentrated hydrochloric acid and 1.5 g. of sodium nitrite dissolved in 30 cc. of water. The solution was added in portions with stirring to a solution of 5.6 g. of copper sulfate in 18 cc. of water, to which had been added 12.0 g. of potassium cyanide in 18 cc. of water. A dark brown material separated, was filtered, removed by ether extraction and crystallized from a small amount of ethyl acetate. The melting point was 115°; yield, 3 g., or 44% of the theoretical.

*Anal.* Calcd. for $C_9H_4OBr_3N$: Br, 62.8. Found: Br, 62.7.

## Summary

The following di-ortho-bromo derivatives of acetophenone have been prepared: 2,4,6-tribromo-3-aminoacetophenone (II), 2,4,6-tribromo-3-hydroxyacetophenone (VII), 2,4,6-tribromo-3-cyanoacetophenone (IX), 2,4,6-tribromophenacyl chloride (VIII) and 2,4,6-tribromoacetophenone (III).

All of these ketones have been treated with solutions of sodium hypochlorite and sodium hypobromite but only two of the corresponding trihalomethyl ketones have been obtained.

2,4,6-Tribromophenacyl chloride has been shown to yield $\alpha,\alpha,\alpha$-trichloro-2,4,6-tribromoacetophenone (V) when treated with solutions of sodium hypochlorite. 2,4,6-Tribromoacetophenone yields the same trichloromethyl derivative when treated with pyridine–sodium hypochlorite solutions. Both 2,4,6-tribromoacetophenone and 2,4,6-tribromophenacyl chloride upon long treatment with sodium hypobromite solutions have been found to yield $\alpha,\alpha,\alpha$-2,4,6-hexabromoacetophenone (IV). Hot concentrated sodium hydroxide solutions caused a very slow decomposition of the trichloromethyl and the tribromomethyl ketones but the normal cleavage product could be isolated only in the first case. Long treatment of 2,4,6-tribromoacetophenone with pyridine–sodium hypohalite solutions caused complete conversion to 2,4,6-tribromobenzoic acid (X).

The results which have been obtained indicate that the two ortho-bromine atoms in these methyl aryl ketones effect a retardation of the haloform reaction which makes it very difficult to effect either the halogena-

tion or the cleavage. Some evidence has been obtained which indicates that the apparent rates of these reactions may be dependent on solubility factors.

URBANA, ILLINOIS

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

# DIHYDRO-1,4-PYRANS. III. THE SYNTHESIS OF THE 1,2-DIBENZOYLCYCLOBUTANES

BY TSI YU KAO AND REYNOLD C. FUSON

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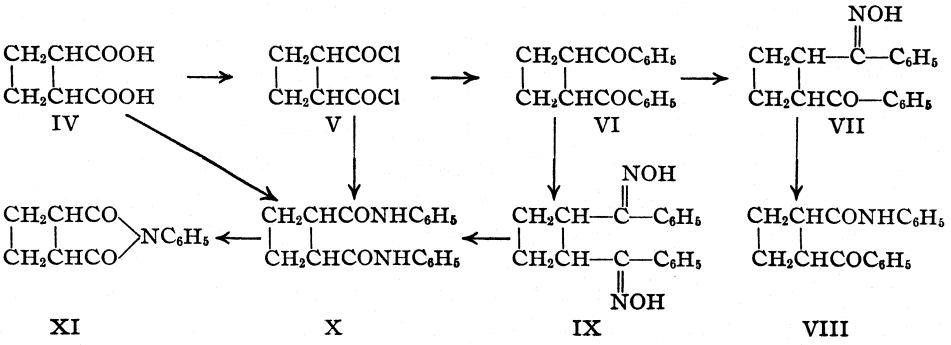
In assigning the structures of the dihydro-1,4-pyrans the alternative formulas considered were 1,2-dibenzoylcyclobutane derivatives.[1] Since these are not known it was determined to synthesize a compound of this type for comparison with the dihydro-1,4-pyrans.

Of the cyclobutane compounds which would offer a direct comparison with the pyrans, 1,2-dibenzoylcyclobutane promised to be easiest to prepare. This compound has now been synthesized and has been found to exist in *cis* and *trans* modifications. This report describes the preparation of these diketones and gives a proof of their structure.

The starting material was the *trans*-1,2-cyclobutanedicarboxylic acid (IV). The *trans* modification of this acid was chosen because it was to be expected that its chloride would be less likely to react in the unsymmetrical form to yield a lactone derivative in the Friedel and Crafts condensation. It was prepared by the methods of Perkin[2] and Fuson and Kao.[3] On treatment with thionyl chloride it gave the corresponding acid chloride (V). This compound when treated with benzene in the presence of aluminum chloride gave two isomeric compounds whose properties corresponded with those predicted for the 1,2-dibenzoylcyclobutane (VI).




[1] Kao and Fuson, THIS JOURNAL, **54**, 313 (1932).

[2] Perkin, *J. Chem. Soc.*, **65**, 585 (1894).

[3] Fuson and Kao, THIS JOURNAL, **51**, 1536 (1929).

The diketone melting at 97° will be called the α-diketone and its isomer melting at 120–121° the β-diketone. Both were found to be insoluble in hot 10% alkali. This excludes the butyrolactone structure because a compound of that type would be soluble in hot alkali. Since the symmetrical diketone can exist in only two forms and since neither of the two isomers obtained is identical with the 1,2-dibenzoylcyclobutane obtained by Conant and Lutz,[4] a proof of the structure was necessary. From the α-diketone were obtained a monoxime (VII) melting at 147–148° and a dioxime (IX) melting at 169–170°. These were transformed into the corresponding anilides by means of the Beckmann rearrangement. The monoanilide (VIII) melted at 130–131°. The dianilide (X) was isolated in two forms which were designated as the α- and β-forms. The α-dianilide melting at 236–236.5° was the principal product of the reaction. The β-dianilide which melted at 219–220° proved to be of more interest because it was found possible to prepare it directly from the original acid, *trans*-1,2-cyclobutanedicarboxylic acid, as well as from the acid chloride of that acid. Moreover, when heated it was transformed into the corresponding phenylimide (XI).[5]

This identification of the dianilide as that of 1,2-cyclobutanedicarboxylic acid establishes the structure of the β-dianilide and leaves no doubt as to the correctness of the structures assigned to the two isomeric diketones. That the latter represent the *cis* and *trans* forms of the 1,2-dibenzoylcyclobutane seems certain but the evidence does not show which is the *cis* and which is the *trans*. Since the starting material was pure *trans*-1,2-cyclobutanedicarboxylic acid, it is evident that an isomerization to the *cis* form must have occurred at some step in the synthesis in order to give rise to the second dibenzoylcyclobutane.

The properties of the α-diketone are such as to show clearly that compounds having this type of structure cannot be confused with the dihydro-1,4-pyrans, for the diketone forms a dioxime and a dibromide—reactions not to be expected of the pyrans. By the principle of exclusion, therefore, this work strongly supports the dihydro-1,4-pyran structures for the products obtained from 1,4-dibromo-1,4-diaroylbutanes by the cyanide ring-closure.

[4] Conant and Lutz, THIS JOURNAL, **49**, 1090 (1927). By reduction of 1,4-dibromo-1,4-dibenzoylbutane with zinc dust a compound melting at 163° was obtained and reported as 1,2-dibenzoylcyclobutane. The structure of this compound was not proved. After this article had been submitted to the Editor, it was found that a third isomer melting at 158–159° (with decomposition) and possibly identical with the diketone of Conant and Lutz, was obtained in small quantity from the mother liquor. This discovery throws doubt on the structure here assigned to the β-diketone since there are now three isomeric forms where but two are theoretically possible. This point is being investigated.

[5] Perkin, *J. Chem. Soc.*, **65**, 584 (1894).

## Experimental

**α-1,2-Dibenzoylcyclobutane.**—Twenty-eight and eight-tenths grams (0.2 mole) of *trans*-1,2-cyclobutanedicarboxylic acid (m. p. 129–130°) was placed in a round-bottomed flask equipped with a condenser. Fifty-nine and one-half grams of thionyl chloride was poured in at once. The mixture was heated gently in a water-bath until solution was complete and the evolution of hydrogen chloride had practically ceased. The flask was then connected through a downward condenser with a water pump. The crude product was heated for a while under diminished pressure to remove any excess thionyl chloride. A mixture of 60 g. of aluminum chloride and 300 cc. of dry benzene was placed in a 3-necked flask fitted with a mercury-sealed stirrer, a condenser and a dropping funnel. The acid chloride obtained as described above was added through the dropping funnel during a period of thirty minutes. The reaction was not allowed to become too vigorous and the temperature was kept below 60°. After the addition of the acid chloride was completed the stirring was continued for two hours longer. During this period the temperature of the reaction mixture was kept at 50–60°.

The reaction mixture darkened in color slowly and was almost black at the end of the reaction. It was poured slowly into 200 g. of cracked ice and 50 cc. of concd. hydrochloric acid. The mixture was stirred vigorously for a few minutes. The benzene layer was decanted and the aqueous solution was extracted two or three times with benzene. The benzene was removed by distillation. The crude product after one recrystallization from 95% ethyl alcohol gave 41.8 g. of an almost pure product melting at 94–97°. The yield was 79.2% of the theoretical. Two more recrystallizations gave fairly large colorless needles melting at 97°. The compound, α-1,2-dibenzoylcyclobutane, was insoluble in boiling 10% sodium hydroxide solution and did not decolorize a warm solution of potassium permanganate.

*Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.6; H, 6.2.

**β-1,2-Dibenzoylcyclobutane.**—The mother liquor from which the α-1,2-dibenzoylcyclobutane was obtained, gave 0.8 g. of a substance which formed fine needles from 95% alcohol and melted at 120–121°. It was insoluble in boiling 10% sodium hydroxide solution and its analysis showed it to be isomeric with the 1,2-dibenzoylcyclobutane.

*Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.4; H, 6.2.

**The Dibromo Derivative of α-1,2-Dibenzoylcyclobutane.**—To a solution of 2.64 g. of α-1,2-dibenzoylcyclobutane in 45 cc. of carbon tetrachloride was added rapidly 3.2 g. of dry bromine. The mixture was shaken vigorously for a few minutes and then allowed to stand for fifteen minutes at room temperature. There was a rapid evolution of hydrogen bromide. The solvent, together with the hydrogen bromide and excess bromine, was then evaporated under diminished pressure. The crude dibromo compound was purified by recrystallization from ethyl acetate. It melted at 148–149°; the yield was 80.6% of the theoretical.

*Anal.* Calcd. for $C_{18}H_{14}O_2Br_2$: Br, 37.9. Found: Br, 37.8.

**The Monoxime of α-1,2-Dibenzoylcyclobutane.**—Five and three-tenths grams of α-1,2-dibenzoylcyclobutane was dissolved in 25 cc. of hydroxylamine hydrochloride solution[6] to which 100 cc. of sodium hydroxide solution[7] was then added. The mixture was heated at 95–100° for one-half hour while it was vigorously stirred. After being cooled the mixture was diluted with 500 cc. of water and acidified with dilute hydro-

[6] Made by dissolving 7.25 g. of hydroxylamine hydrochloride in 9 cc. of water and diluting with ethyl alcohol to 35 cc.

[7] Prepared by dissolving 10 g. of sodium hydroxide in 20 cc. of water and diluting with alcohol to 140 cc.

chloric acid. The monoxime was obtained as a yellow gummy substance which after repeated recrystallization from 95% ethyl alcohol separated in clusters of large needles melting at 147–148°.

*Anal.* Calcd. for $C_{18}H_{17}NO_2$: C, 77.4; H, 6.1. Found: C, 77.3; H, 6.1.

**The Anilide of 2-Benzoyl-1-cyclobutanecarboxylic Acid.**—One gram of the monoxime was added to a mixture of 3 cc. of thionyl chloride and 7 cc. of chloroform in a small Erlenmeyer flask surrounded with cracked ice. The mixture was thoroughly shaken, allowed to stand in the ice water-bath for a few minutes and then at room temperature for one hour. Some cracked ice was added to the reaction mixture. The chloroform layer was separated and washed with a little water. The chloroform was removed and the solid which remained was dried on a clay plate and recrystallized from 95% alcohol. In this way 0.4 g. of fine long needles melting at 130–131° was obtained.

*Anal.* Calcd. for $C_{18}H_{17}NO_2$: C, 77.4; H, 6.1. Found: C, 76.8; H, 6.2.

**The Dioxime of α-1,2-Dibenzoylcyclobutane.**—Six grams of α-1,2-dibenzoylcyclobutane was dissolved in 60 cc. of absolute alcohol. To this solution a mixture of 6.0 g. of hydroxylamine hydrochloride and 12.0 g. of potassium acetate in 50 cc. of water was added. The mixture was refluxed for half an hour. It was then allowed to stand at room temperature in an open flask. Crystals collected on the bottom of the flask. The liquor was decanted into another flask and the crystals were filtered and washed with water. After a few days the mother liquor deposited a second crop of crystals. Sometimes a third or even fourth crop of crystals was obtained. The combined crude product amounting to 3.8 g. melted at 160–164°. After two or three recrystallizations from 95% alcohol it melted at 169–170°.

*Anal.* Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.4; H, 6.2. Found: C, 73.4; H, 6.3.

### Dianilides of 1,2-Cyclobutanedicarboxylic Acid

**A. By the Beckmann Rearrangement of 1,2-Dibenzoylcyclobutane Dioxime.**—Seven-tenths of a gram of the dioxime was dissolved in 14 cc. of chloroform. This solution was cooled to 0° and 6 cc. of thionyl chloride was added. The mixture had a yellow color at first and later turned red. At the end of an hour the reaction mixture was decomposed with ice. Twenty cc. of chloroform was added and the chloroform solution was separated from the aqueous layer. There was obtained 0.2 g. of a product melting at 234–236°. After it was recrystallized from 95% alcohol the α-dianilide melted at 236–236.5°. A small amount of a different substance was obtained from the mother liquor. This compound which has been called the β-dianilide was isomeric with the α-dianilide but was different from it in crystalline form. The β-dianilide melted at 219–220°.

*Anal.* Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.4; H, 6.2; N, 9.5. Found: α-dianilide: C, 73.1; H, 6.6. β-dianilide: C, 73.5; H, 6.3; N, 9.6.

**B. By Heating *Trans*-1,2-cyclobutanedicarboxylic Acid with Aniline.**—Four and three-tenths grams of *trans*-1,2-cyclobutanedicarboxylic acid was heated in a test-tube with 11.2 g. of pure aniline at 150–160° for three hours. Water was given off when the temperature reached 140°. The dark mass was ground in a mortar with 20 cc. of dilute hydrochloric acid. It was filtered, ground with hydrochloric acid once more, filtered again and washed several times with water. In this way 7.41 g. of product melting at 219–220° was obtained. The yield was 84% of the theoretical. This product was identified as the β-dianilide by the method of mixed melting points.

**C. By the Reaction of *Trans*-1,2-cyclobutanedicarboxylic Acid Chloride and Aniline.**—One and four-tenths grams of *trans*-1,2-cyclobutanedicarboxylic acid was mixed with 2.5 g. of phosphorus pentachloride and warmed at 70° for a few minutes. The

acid chloride thus obtained was poured drop by drop into 10 cc. of aniline. The reaction mixture solidified on cooling and was purified as described in B. By recrystallization of the product from 95% alcohol 2.2 g. of the β-dianilide was obtained. The yield was 75% of the theoretical.

**Phenylimide of 1,2-Cyclobutanedicarboxylic Acid.**—Two grams of the β-dianilide of 1,2-cyclobutanedicarboxylic acid was heated in a test-tube. The temperature was raised slowly until aniline began to come off. This took place at a temperature of about 240°. The mixture was then maintained at 240–250° for sixteen hours. The contents of the test-tube was dissolved in alcohol, boiled with animal charcoal and filtered. The filtrate, on being allowed to cool, deposited long needles, melting at 126.5–127°. The yield of the imide was 1 g. or 73% of the theoretical.

## Summary

The acid chloride of *trans*-1,2-cyclobutanedicarboxylic acid has been shown to react normally with benzene in the presence of aluminum chloride to give a mixture of the *cis* and *trans* forms of 1,2-dibenzoylcyclobutane.

The structure of one of these diketones has been proved by its transformation successively into the dioxime and the corresponding dianilide, which in turn has been shown to be that of 1,2-cyclobutanedicarboxylic acid.

In their reactions these compounds differ widely from the isomeric dihydro-1,4-pyran derivatives. The cyclobutane structures previously considered for the latter compounds are, accordingly, eliminated as possibilities. By the exclusion principle, therefore, the present work strongly supports the dihydro-1,4-pyran structures for the derivatives obtained from 1,4-dibromo-1,4-diaroylbutanes by the cyanide ring-closure.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# THE PINACOL–PINACOLIN REARRANGEMENT. THE RELATIVE MIGRATION APTITUDES OF ARYL GROUPS[1]

BY W. E. BACHMANN AND FRANK H. MOSER

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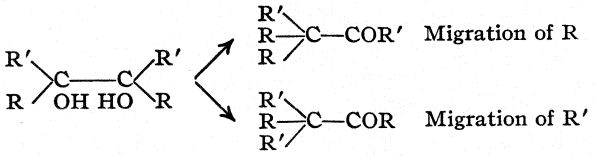
The rearrangement of symmetrical mixed pinacols of the type RR′-(OH)C—C(OH)RR′ has been recognized as one of the best means of comparing migration aptitudes[2] of groups since the groups are in structurally identical positions. Moreover, the nature of the pinacolin which is formed indicates which of the two groups has migrated. The two possibilities may be represented as follows:

[1] The material here presented is from a dissertation submitted by Frank H. Moser to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1931.

[2] See Tiffeneau and Orekhoff, *Bull. soc. chim.*, **35**, 1639 (1924), and *Ann. Reports*, **27**, 114 (1930), for reviews of the subject.




The study of this rearrangement has been retarded by the lack of good methods for preparing pinacols. The new reaction of Gomberg and Bachmann[3] involving the reduction of ketones by a mixture of magnesium and magnesium iodide has stimulated interest in the pinacol rearrangement, for the reaction has proved to be an excellent method for making symmetrical aromatic pinacols. We have employed this method for synthesizing pinacols containing aryl groups whose migration aptitudes we wished to determine.

We desired particularly to determine whether the migration aptitudes of two groups in a symmetrical pinacol are properties of the groups themselves or are dependent on the particular molecule in which they happen to be found. If the migration aptitudes depend only on the groups, then it should be possible, knowing the relative migration aptitude of group $R_1$ to $R_2$ and of $R_1$ to $R_3$, to predict the course of rearrangement of a pinacol containing the groups $R_2$ and $R_3$. Accordingly, we synthesized and rearranged those pinacols which allowed us to make predictions of this kind, and we then proceeded to check these predictions by experiment. We found that the predicted values agreed with the experimental results, indicating that *in symmetrical aromatic pinacols* the nature of the rearrangement depends upon the characteristic groups present.

## Experimental

**Reduction of Ketones by Magnesium + Magnesium Iodide.**—Eleven ketones were reduced to pinacols by the reaction of Gomberg and Bachmann. The quantity of metallic magnesium that reacted with a given amount of ketone and magnesium iodide corresponded to that required by the formulation: $2RR'CO + Mg + MgI_2 \longrightarrow 2RR'COMgI \rightleftharpoons (RR'COMgI)_2$. In every case the reaction proceeded through the intermediate formation of free ketyl radicals, as was indicated by the color and by the reactions[3] of the solution. The colors of the ketyl varied from red to purple. On exposure to air these colors disappeared, but they appeared again when air was excluded. The behavior of these radicals with iodine and with oxygen was studied and, as a rule, a large yield of ketone was produced. For all of the pinacols, the identical equilibrium mixture, ketyl $\rightleftharpoons$ pinacolate, was obtained by the action of the Grignard reagent on the pinacol as resulted from the ketone and the binary system. In Table I are given the yields and the melting points of the pinacols which were obtained by hydrolysis of the iodomagnesium pinacolates.

In the preparation of the pinacols several new ketones were synthesized, all by means of the Friedel and Crafts reaction from biphenyl and the required acid chloride.

**3-Methyl-4′-phenylbenzophenone.**—Yield, 77%; b. p. 234° at 10 mm.; **m. p.** 80–81°. The ketone was recrystallized by dissolving it in a small amount of chloro-

[3] Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927).

TABLE I

PINACOLS OBTAINED BY REDUCTION OF KETONES BY Mg + $MgI_2$

| Benzopinacol | Yield, % | M. p., °C. |
|---|---|---|
| *Sym.*-4,4'-dimethyl- | 96 | 173 |
| *Sym.*-4,4'-dimethyl-4'',4'''-diphenyl-[a] | 93 | 180–182 |
| *Sym.*-3,3'-dimethyl- | 82 | 151–152 |
| **Sym.*-3,3'-dimethyl-4'',4'''-diphenyl-[b] | 96 | 174–175 |
| *Sym.*-2,2'-dimethyl- | 22 | 167 |
| **Sym.*-2,2'-dimethyl-4'',4'''-diphenyl-[c] | 35 | 182–183 |
| *Sym.*-4,4'-dimethoxy-[d] | 45 | 173–174 |
| **Sym.*-4,4'-dimethoxy-4'',4'''-dimethyl-[e] | 4 | 175–176 |
| **Sym.*-4,4'-dimethoxy-4'',4'''-diphenyl-[f] | 22 | 172–174 |
| *Sym.*-4,4'-dichloro-4'',4'''-dimethyl- | 89 | 175–176 |
| **Sym.*-4,4'-dichloro-4'',4'''-diphenyl-[g] | 98 | 190–191 |

* New pinacols.

[a] The solution containing the ketyl is red by transmitted light and blue by reflected light. Bailar, THIS JOURNAL, **52**, 3596 (1930), reported 175–176° as the melting point of this pinacol.

[b] The ketyl solution has a wine color by transmitted light and is dark blue by reflected light. The pinacol was recrystallized from a mixture of benzene and petroleum ether. *Anal.* Calcd. for $C_{40}H_{34}O_2$: C, 87.87; H, 6.27. Found: C, 88.30; H, 6.22.

[c] The color of the ketyl is dark purple. The pinacol crystallized well from a mixture of benzene and petroleum ether. *Anal.* Calcd. for $C_{40}H_{34}O_2$: C, 87.87; H, 6.27. Found: C, 87.66; H, 6.35.

[d] The ketyl is blood red in color. The pinacol crystallized from a mixture of benzene and alcohol in the form of glistening diamond-like crystals. Reduction of 5 g. of 4-methoxybenzophenone with zinc dust and acetic acid in the cold gave 4.4 g. (88%) of the same pinacol. Using the same reducing mixture, Tiffeneau and Orékhoff, *Bull. soc. chim.*, **37**, 430 (1925), obtained only pinacolin (m. p. 125–126°); this was undoubtedly due to the fact that they heated the reduction mixture, thereby causing a rearrangement to take place.

[e] The ketyl is blood red in color. The pinacol was recrystallized from a mixture of benzene and alcohol. *Anal.* Calcd. for $C_{30}H_{30}O_4$: C, 79.25; H, 6.66. Found: C, 79.20; H, 6.54. By allowing a mixture of 5 g. of 4-methoxy-4'-methylbenzophenone, 55 cc. of acetic acid and 10 g. of zinc dust to stand at room temperature for three days, 4.65 g. (93%) of the same pinacol was obtained. Employing the same reaction but heating the mixture, Orékhoff and Brouty, *Bull. soc. chim.*, **47**, 621 (1930), obtained a product melting at 130–131° which they considered was pinacol. They obtained the same product by the action of *p*-tolylmagnesium bromide on anisil; we tried this reaction and obtained only the pinacol of melting point 175–176°. It should be noted that the pinacolin which is obtained on rearrangement of our pinacol melts at 130–131°.

[f] The ketyl solution was bright red in color. Large losses of pinacol occurred in recrystallization. The pinacol was also prepared by the action of anisylmagnesium bromide on 4,4'-diphenylbenzil. *Anal.* Calcd. for $C_{40}H_{34}O_4$: C, 83.01; H, 5.93. Found: C, 83.59; H, 5.92.

[g] The ketyl was dark red in color. The pinacol crystallized from a mixture of carbon tetrachloride and alcohol in small colorless granules. *Anal.* Calcd. for $C_{38}H_{28}Cl_2O_2$: Cl, 12.08. Found: Cl, 12.06, 12.02.

form and adding alcohol. It is extremely soluble in benzene, ether, carbon tetrachloride, chloroform and acetone in the cold. It is very soluble in hot alcohol but not very soluble in the cold.

*Anal.* Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.93; H, 5.82.

**2-Methyl-4'-phenylbenzophenone.**—Yield, 88%; b. p. 283–285° (20 mm.). It crystallized from alcohol in glistening white plates; m. p. 107–109°.

*Anal.* Calcd. for $C_{20}H_{16}O$: C, 88.28; H, 5.92. Found: C, 88.28; H, 5.89.

**4-Methoxy-4'-phenylbenzophenone.**—Yield, 35%. The product crystallizes from benzene in colorless flakes; m. p. 165–167°.

*Anal.* Calcd. for $C_{20}H_{16}O_2$: C, 83.30; H, 5.59. Found: C, 83.41; H, 5.54.

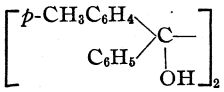
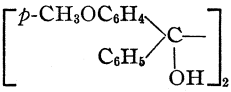
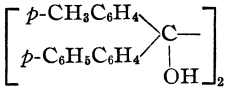
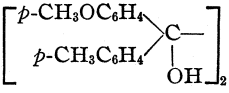
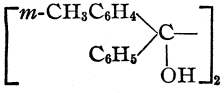
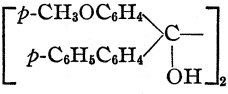
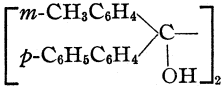
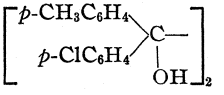
**4-Chloro-4'-phenylbenzophenone.**—Yield, 79%; b. p. 300° (10 mm.). The ketone crystallized from chlorobenzene in light fluffy plates.

*Anal.* Calcd. for $C_{19}H_{13}ClO$: Cl, 12.12. Found: Cl, 12.15, 11.92.

**Rearrangement of Pinacols. Comparison of Migration Aptitudes.**—Since there is some question whether the nature of the rearranging medium has an effect on the course of the rearrangement, all of the pinacols were rearranged with the same rearranging mixture. This consisted of a mixture of acetyl chloride, acetic acid and benzene; it has a good solvent action as well as a higher boiling point than acetyl chloride alone. Several runs were made on each pinacol and the results checked each other closely. The nature and amounts of the pinacolins which were formed were found in each case by scission of the pinacolins into triarylmethanes and acids by the reaction: $R_3CCOR + KOH \longrightarrow R_3CH + KOOCR$. In some cases the mixture of acids so formed was resolved into its components by taking advantage of the differences in their solubilities. The yields of acids varied between 90–99%. Usually the methane formed in the larger amount was isolated in a pure state. The results of the rearrangements are summarized in Table II.

TABLE II

MIGRATION OF GROUPS

| Pinacol | Groups | Migration, % | Pinacol | Groups | Migration, % |
|---|---|---|---|---|---|
|  | *p*-Tolyl | 94 |  | Anisyl | 98.6 |
| | Phenyl | 6 | | Phenyl | 1.4 |
|  | *p*-Tolyl | 57 |  | Anisyl | 96.7 |
| | *p*-Biphenyl | 43 | | *p*-Tolyl | 3.3 |
|  | *m*-Tolyl | 66 |  | Anisyl | 96.8 |
| | Phenyl | 34 | | *p*-Biphenyl | 3.2 |
|  | *m*-Tolyl | 13 |  | *p*-Tolyl | 82 |
| | *p*-Biphenyl | 87 | | *p*-Chlorophenyl | ? |

Several of the pinacols which were rearranged are not listed in the table because the reactions were not complete. It is noteworthy that in every rearrangement that could be studied quantitatively both of the groups migrated. In several cases, previous investigators had reported that only one group of a particular pinacol had migrated.

**General Procedure for Rearrangement and Scission.**—One hundredth of a gram mole of pinacol was placed in a 200-cc. round-bottomed flask connected by a ground-glass joint to a condenser, and a mixture of 40 cc. of acetyl chloride, 20 cc. of glacial

acetic acid and 80 cc. of benzene was added. The solution was refluxed on a steam-bath for a varying period of time (depending on the pinacol). The solvents were distilled off under reduced pressure and a solution of 6 g. of potassium hydroxide in 100 cc. of absolute alcohol was added. Refluxing was carried on until the splitting of the pinacolins was complete. The alcohol was then distilled off and 100 cc. of water was added; this dissolved the potassium salts of the organic acids while the methanes were present as precipitates. The methanes were extracted from the aqueous solution with benzene three times and the benzene was allowed to evaporate in order to obtain the methanes. The aqueous solution was acidified with hydrochloric acid and was extracted with benzene in order to get out all organic acids.

**4,4′-Dimethylbenzopinacol.**—The rearrangement was allowed to proceed for thirty-six hours; the splitting reaction proceeded for six days. Thörner and Zincke[4] reported that the acid obtained was for the most part benzoic acid since it melted only a few degrees lower than pure benzoic acid; as a result they reported that the *p*-tolyl group migrated exclusively. It was found impossible to separate a mixture of 95% of benzoic acid and 5% of toluic acid into its components by means of the difference in solubility of the two acids. A determination of the amount of *p*-toluic acid was obtained by oxidizing it to terephthalic acid, which is practically insoluble in water and which can therefore be easily separated from the more soluble benzoic acid. The mixture of acids was heated for one-half hour with 1 g. of potassium dichromate, 3 cc. of sulfuric acid and 6 cc. of water. A correction for the losses occurring during oxidation was determined by oxidizing several synthetic mixtures of benzoic acid and *p*-toluic acid of approximately the same composition in the same manner. The methane obtained on recrystallization of the crude product was identified as 4,4′-dimethyltriphenylmethane.

**4,4′-Dimethyl-4″,4‴-diphenylbenzopinacol.**—Time for rearrangement, thirty-six hours; time for scission, six days. The acids were separated by virtue of the slight solubility of *p*-phenylbenzoic acid in hot water. A correction for its solubility was made by treating similar mixtures of *p*-phenylbenzoic acid and *p*-toluic acid in the same manner. Bailar[5] found equal quantities of the two pinacolins; he used acetic acid and iodine as the rearranging agent and determined the proportions of the two acids in the mixture by a determination of the equivalent weight.

The mixture of methanes weighed 2.58 g. and was resolved into its two components by dissolving the mixture in 20 cc. of warm ether. Upon cooling, 1.13 g. of 4,4′-diphenyl-4″-methyltriphenylmethane (synthesis given below) crystallized out; m. p. 160–162°. From the filtrate 0.74 g. of 4-phenyl-4′,4″-dimethyltriphenylmethane was obtained; m. p. 123–125°. The same melting point was observed when this substance was mixed with synthetic 4-phenyl-4′,4″-dimethyltriphenylmethane.

**1,1-Dibiphenyl-1,2-di-*p*-tolylethanone-2.**—It was possible to isolate this pinacolin from the mixture because of its slight solubility in organic solvents. Two grams of *sym.*-4,4′-dimethyl-4″,4‴-diphenylbenzopinacol was heated for twelve minutes with 15 cc. of glacial acetic acid containing a crystal of iodine. A yield of 0.58 g. (30%) of colorless crystals melting at 227–229° was obtained. The structure of these crystals was proved by quantitative scission into 4-methyl-4′,4″-diphenyltriphenylmethane and *p*-toluic acid.

*Anal.* Calcd. for $C_{40}H_{32}O$: C, 90.87; H, 6.11. Found: C, 91.18; H, 6.02.

**4,4′-Diphenyl-4″-methyltriphenylcarbinol.**—This carbinol was synthesized from *p*-tolylmagnesium bromide and dibiphenyl ketone; yield, 58%. The compound

[4] Thörner and Zincke, *Ber.*, **10**, 1473 (1877); **11**, 65 (1778).

[5] Bailar, THIS JOURNAL, **52**, 3596 (1930).

crystallized from a mixture of ether and benzene in fine colorless crystals; m. p. 143–144°; it gives a red color with concentrated sulfuric acid.

*Anal.* Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.15. Found: C, 90.24; H, 6.10.

**4,4′-Diphenyl-4″-methyltriphenylmethane.**—The carbinol was reduced to the methane by heating it with zinc and acetic acid. The methane crystallized in fine colorless needles from benzene; m. p. 162–163°.

*Anal.* Calcd. for $C_{32}H_{26}$: C, 93.61; H, 6.39. Found: C, 93.97; H, 6.37.

**4,4′-Dimethyl-4″-phenyltriphenylmethane.**—The corresponding carbinol was prepared from *p*-tolylmagnesium bromide and *p*-tolyl biphenyl ketone; the product was an oil which did not crystallize. It was reduced by zinc and acetic acid to the methane. On recrystallization from ether the methane was obtained in the form of colorless needles which melted at 123–125°.

*Anal.* Calcd. for $C_{27}H_{24}$: C, 93.05; H, 6.95. Found: C, 93.02; H, 6.99.

**3,3′-Dimethylbenzopinacol.**—Time for rearrangement, three hours; time allowed for scission, one day. The mixture of acids was dissolved in a solution of 1 g. of potassium hydroxide in 50 cc. of water, 1.4 g. of powdered potassium permanganate was added and the solution was heated for one hour on a steam-bath. This treatment oxidized the *m*-toluic acid to isophthalic acid and left the benzoic acid unchanged; the benzoic acid was then extracted from the mixture by means of water. As usual, a correction for the solubility of the isophthalic acid was determined by oxidation of a synthetic mixture of benzoic and *m*-toluic acids. From the mixtures of methanes, crystals of 3-methyltriphenylmethane were isolated and identified by a mixed melting point determination with an authentic specimen.

Recently Bailar determined the migration aptitudes of the phenyl and *m*-tolyl groups and reported that the *m*-tolyl group migrated 37 to 63% for the phenyl group, values that are practically the reverse of ours. He did not separate the two acids but determined the equivalent weight of the mixture. We repeated the rearrangement, used that method of analysis and confirmed our results. Bailar employed a mixture of acetic acid and iodine for rearranging the pinacol.

**3,3′-Dimethyl-4″,4‴-diphenylbenzopinacol.**—Twenty-four hours were allowed for rearrangement while seven days were given for splitting. The mixture of acids was resolved by making use of the solubility of *m*-toluic acid in hot water. By recrystallization of the methanes (2.72 g.), pure 3-methyl-4′,4″-diphenyltriphenylmethane was obtained; its structure was confirmed by synthesis.

**3-Methyl-4′,4″-diphenyltriphenylcarbinol.**—This new carbinol was prepared by refluxing a mixture of 6.7 g. of dibiphenyl ketone suspended in 100 cc. of benzene with the Grignard reagent from 7.25 g. of *m*-bromotoluene. The carbinol crystallized from a mixture of benzene and petroleum ether in small colorless rods; m. p. 124–125°; yield, 5.32 g. The compound gives a red color with concentrated sulfuric acid.

*Anal.* Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.15. Found: C, 89.88; H, 6.23.

**3-Methyl-4′,4″-diphenyltriphenylmethane.**—Two grams of carbinol was heated with zinc and a mixture of acetic and hydrochloric acids (6:1) for two hours; yield of methane, 1 g. It was recrystallized by adding petroleum ether to a hot saturated benzene solution; m. p. 144–145°. No change in melting point was observed when this substance was mixed with the methane obtained by scission of the pinacolins.

*Anal.* Calcd. for $C_{32}H_{26}$: C, 93.61; H, 6.39. Found: C, 93.35; H, 6.49.

**4,4′-Dimethoxybenzopinacol.**—Time allowed: for rearrangement, twenty-four hours; for scission, two days. In order to determine the amount of anisic acid present in the mixture of acids, a methoxyl estimation was made. Trial runs using synthetic mixtures gave good results. Recrystallization of the crude methanes gave pure 4,4′-

dimethoxytriphenylmethane of m. p. 100–101°, confirming the results obtained by analysis of the acid mixture. Tiffeneau and Orékhoff[6] have reported that the anisyl group migrates exclusively in preference to the phenyl group. Our more careful method of analysis shows that the phenyl group migrates to the extent of 1.4%.

**4,4′-Dimethoxy-4″,4‴-dimethylbenzopinacol.**—Time required: for rearrangement, two hours; for splitting, three days. The mixture of acids was analyzed for anisic acid by making a methoxyl determination. Recrystallization of the methane from a mixture of ether and petroleum ether gave white fibers of dianisyl-*p*-tolylmethane, melting at 45–46°. Orékhoff and Brouty[7] report 40–42° for this value. These investigators reported that the anisyl group migrates exclusively with respect to the *p*-tolyl group, while our results show that the *p*-tolyl group migrates to the extent of 3.3%. It appears that they recrystallized the crude pinacolin mixture before splitting it.

**1,1-Dianisyl-1,2-di-*p*-tolyl-ethanone-2.**—Inasmuch as the rearrangement of the pinacol gave this pinacolin to the extent of 96%, we were able to isolate it easily in a pure state by recrystallizing the crude mixture of pinacolins; yield, 80%; m. p. 129–130°. Orékhoff and Brouty reported a melting point of 81° for this pinacolin.

*Anal.* Calcd. for $C_{30}H_{26}O_3$: C, 82.53; H, 6.47. Found: C, 82.40; H, 6.54.

**4,4′-Dimethoxy-4″,4‴-diphenylbenzopinacol.**—Time allowed: for rearrangement, two hours; for splitting, eleven days. A methoxyl determination was run on the mixture of acids; the material remaining after the determination was found to be principally *p*-phenylbenzoic acid. Recrystallization of the methanes from a mixture of benzene and petroleum ether gave a product of m. p. 118–119° which was proved by synthesis to be 4,4′-dimethoxy-4″-phenyltriphenylmethane.

**4,4′Dimethoxy-4″-phenyltriphenylmethane.**—The carbinol was prepared by the action of anisylmagnesium bromide on 4-methoxy-4′-phenylbenzophenone; the product could not be made to crystallize. Two grams of the oily carbinol was reduced to the corresponding methane by heating it with 35 cc. of formic acid[8] for two days. The product was recrystallized from benzene and petroleum ether and was obtained in clusters of diamond-shaped crystals; m. p. 118–119°; yield, 0.59 g.

*Anal.* Calcd. for $C_{27}H_{24}O_2$: C, 85.22; H, 6.36. Found: C, 85.43; H, 6.28.

**4,4′-Dichloro-4″,4‴-dimethylbenzopinacol.**—The pinacol was heated with the rearranging mixture for sixty-six hours; the scission reaction mixture was refluxed for five days; 200 cc. of alcohol was used in order to get the pinacolin completely in solution. A 52% yield of practically pure *p*-chlorobenzoic acid (m. p. 230–232°) was isolated; in addition, a 30% yield of unchanged pinacolin, which proved to be 1,1-di-*p*-tolyl-1,2-di-*p*-chlorophenylethanone-2, was obtained. These results show that, although the scission was not complete, at least 82% migration of the *p*-tolyl group had occurred. A small amount of pure 4-chloro-4′,4″-dimethyltriphenylmethane was isolated; it was identified by comparison with a synthetic product.

**1,1-Di-*p*-tolyl-1,2-di-*p*-chlorophenylethanone-2.**—This pinacolin was the principal product of the rearrangement of *sym.*-dichlorodimethylbenzopinacol; after recrystallization from alcohol it melted at 204–205°. Its structure was proved by scission into 4-chloro-4′,4″-dimethyltriphenylmethane and *p*-chlorobenzoic acid; this splitting, however, was not quantitative.

*Anal.* Calcd. for $C_{28}H_{22}OCl_2$: Cl, 15.93. Found: Cl, 15.74, 16.13.

**4-Chloro-4′,4″-dimethyltriphenylcarbinol.**—This carbinol was prepared by the action of *p*-tolylmagnesium bromide on 4-chloro-4′-methylbenzophenone; the product

[6] Tiffeneau and Orékhoff, *Bull. soc. chim.*, **37**, 430 (1925).

[7] Orékhoff and Brouty, *ibid.*, **47**, 621 (1930).

[8] Kaufmann and Panwitz, *Ber.*, **45**, 769 (1912).

was recrystallized from petroleum ether; m. p. 94–95°; yield, 62%. The carbinol gives an orange color with concentrated sulfuric acid.

*Anal.* Calcd. for $C_{21}H_{19}ClO$: Cl, 10.99. Found, Cl, 11.01, 10.90.

**4-Chloro-4′,4″-dimethyltriphenylmethane.**—A mixture of 1.22 g. of carbinol and 30 cc. of formic acid was heated on a steam-bath for fourteen hours. The methane which was obtained on diluting the reaction mixture with water was recrystallized from petroleum ether and was obtained as colorless, granular crystals melting at 66–68°; yield, 0.52 g.

*Anal.* Calcd. for $C_{21}H_{19}Cl$: Cl, 11.57. Found: Cl, 11.51, 11.94.

**4,4′-Dichloro-4″,4‴-diphenylbenzopinacol.**—Time allowed: for rearrangement, twenty-four hours; for scission, nine days. Only 0.10 g. of acid (*p*-chlorobenzoic acid) was obtained. Splitting of the pinacolin was not accomplished by heating it with potassium hydroxide in a sealed tube at 150°. The pinacolin, undoubtedly 1,1-dibiphenyl-1,2-di-*p*-chlorophenylethanone-2, was recrystallized twice from benzene and melted at 250–255°. Koopal[9] experienced similar difficulties in attempting to split halogen substituted pinacolins.

**2,2′-Dimethylbenzopinacol.**—Hatt[10] reported that this pinacol was rearranged by warming it with acetic acid and iodine. Bailar, however, was unable to rearrange this pinacol and explained the lack of rearrangement on the basis of affinity capacities. We obtained an uncrystallizable resin-like product when we used acetyl chloride for rearrangement. The resinous product was not cleaved by potassium hydroxide. However, heating the resin with acetic acid and iodine converted it to a pinacolin which gave *o*-toluic acid (63% yield), indicating migration of the phenyl group.

**2,2′-Dimethyl-4″,4‴-diphenylbenzopinacol.**—Treatment of the pinacol with the customary rearranging mixture gave a transparent resin which was not split by potassium hydroxide. Hot acetic acid and iodine converted this resin to pinacolin which gave *o*-toluic acid on scission with alkali; this shows that the biphenyl group migrated in preference to the *o*-toyl group.

**2-Methylbenzopinacol.**—After our unsuccessful attempts to rearrange pinacols containing two *o*-methyl groups, by means of acetyl chloride, we attempted the rearrangement of a pinacol with only one *o*-methyl group. However, there resulted a resinous product which was not cleaved by potassium hydroxide. Acetic acid and iodine converted the resin to pinacolin which on scission gave a 93% yield of a mixture of acids consisting chiefly of benzoic acid.

This new pinacol was synthesized as follows. The Grignard reagent prepared from 19 g. of *o*-bromotoluene and 2.4 g. of magnesium in 40 cc. of ether was added to a solution of 21.0 g. of benzil and the resulting mixture was allowed to stand for twenty-four hours. The product obtained by hydrolysis of the reaction mixture was dissolved in 100 cc. of benzene and this solution was added to the Grignard reagent which had been prepared from 50 g. of bromobenzene in 100 cc. of ether. The solution was refluxed for three hours and was then allowed to stand for twelve hours. Upon hydrolysis the pinacol was obtained as a colorless solid. It was recrystallized from chloroform; yield, 14 g.; m. p. 175–176°.

*Anal.* Calcd. for $C_{27}H_{24}O_2$: C, 85.22; H, 6.36; Found: C, 84.73; H, 6.41.

## Discussion

**Predicting Migration Aptitudes.**—The method of predicting the relative migration aptitudes of two groups from the values of the relative

[9] Koopal, *Rec. trav. chim.*, **34**, 115 (1915).

[10] Hatt, *J. Chem. Soc.*, 1633 (1929).

migrations of each of these groups with respect to a third mutual group may be illustrated by an example. The rearrangement of a phenyl-*p*-tolyl pinacol gave the following results: *p*-$CH_3C_6H_4$ (94%) : $C_6H_5$ (6%). Rearrangement of the pinacol containing the *p*-biphenyl[3] and phenyl groups gave the relation: *p*-$C_6H_5C_6H_4$ (92%), $C_6H_5$ (8%). Then the relative migration aptitudes of the *p*-tolyl group with respect to the biphenyl group is found as follows

$$\frac{p\text{-}CH_3C_6H_4}{p\text{-}C_6H_5C_6H_4} = \frac{p\text{-}CH_3C_6H_4/C_6H_5}{p\text{-}C_6H_5C_6H_4/C_6H_5} = \frac{94/6}{92/8} = \frac{58}{42}$$

This means that the pinacol containing the *p*-tolyl and the *p*-biphenyl groups should rearrange with 58% migration of the *p*-tolyl group and 42% migration of the *p*-biphenyl group. The values found experimentally are: *p*-$CH_3C_6H_4$ (57%) and *p*-$C_6H_5C_6H_4$ (43%).

In Table III the predicted values for the rearrangement of a number of pinacols are compared with the experimental results. The group in parentheses is the mutual group employed in the calculation of the predicted values.

TABLE III

MIGRATION OF GROUPS

| Groups | | Predicted, % | Found, % |
|---|---|---|---|
| *p*-Tolyl | (Phenyl) | 58 | 57 |
| *p*-Biphenyl | | 42 | 43 |
| *m*-Tolyl | (*p*-Biphenyl) | 63 | 66 |
| Phenyl | | 37 | 34 |
| Anisyl | (*p*-Tolyl) | 97.5 | 96.8 |
| *p*-Biphenyl | | 2.5 | 3.2 |
| Anisyl | (*p*-Tolyl) | 99.8 | 98.6 |
| Phenyl | | 0.2 | 1.4 |
| *p*-Bromophenyl[a] | (Phenyl) | 6.0 | 4.5 |
| *p*-Biphenyl | | 94.0 | 95.5 |
| *p*-Ethylphenyl[b] | (Phenyl) | 24 | 25 |
| *p*-Tolyl | | 76 | 75 |
| Anisyl[b] | (*p*-Tolyl) | 96.3 | 67 |
| α-Naphthyl | | 3.7 | 33 |

[a] From results of Gomberg and Bailar, THIS JOURNAL, 51, 2229 (1929). These investigators found that predictions in two instances were verified by experiment.

[b] From results of Bailar, Table I, Ref. *a*.

It is seen that the predicted values in all but one case (anisyl-α-naphthyl) agree satisfactorily with the experimental values. Other predictions can be made and we are continuing our work of checking them by experiment.

Tiffeneau and Orékhoff assigned to the individual groups a value representing its migration aptitude with respect to the phenyl group as a standard. The series was recently amplified by Bailar. In view of our results we obtain the following order and values: anisyl, 70 or more; α-

naphthyl, 18; *p*-tolyl, 15; *p*-biphenyl, 11.5; *p*-isopropylphenyl, 9; *p*-ethylphenyl, 5; *m*-tolyl, 1.95; *p*-fluorophenyl, 1.85; *p*-iodophenyl, 1; phenyl, 1; *p*-bromophenyl, 0.71; *p*-chlorophenyl, 0.66; *m*-methoxyphenyl, 0.2; *o*-tolyl, *o*- and *m*-bromophenyl and *o*- and *m*-chlorophenyl, very small. It should be noted that the series of migration aptitudes coincides well with a similar series of affinity capacities of the same groups; this is in harmony with the observation of Tiffeneau and Orekhoff that the groups that have the greatest affinity capacity migrate most easily.


## Summary

A number of pinacols have been prepared by the reaction of Gomberg and Bachmann and a study has been made of the equilibrium mixture, ketyl $\rightleftarrows$ pinacolate, which is found in each case.

Twelve pinacols have been subjected to the pinacol–pinacolin rearrangement and a comparison of the migration aptitudes of the phenyl, *p*-tolyl, *p*-biphenyl, anisyl, *o*-tolyl, *m*-tolyl and *p*-chlorophenyl groups has been obtained.

The migration aptitudes of a group *in a symmetrical benzopinacol* has been shown to be a property characteristic of that group and is not dependent on the particular pinacol in which it is found.


ANN ARBOR, MICHIGAN

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# OXIDATION OF UNSATURATED COMPOUNDS. VI. SYNTHESIS OF 3-BROMOTHREONIC ACID. SUPPLEMENT TO THE PROOF OF CONFIGURATION OF *dl*-1,2-DIHYDROXYBUTYRIC ACIDS

BY GÉZA BRAUN[1]

RECEIVED OCTOBER 15, 1931 PUBLISHED MARCH 5, 1932

In a recent publication of this series the proof of configuration of *dl*-1,2-dihydroxybutyric acids was presented.[2] The proof was based on the fact that the 3-chlorothreonic acid could be converted into racemic tartaric acid and on the other hand it could be reduced to the *dl*-1,2-dihydroxybutyric acid (m. p. 74°), which shows clearly that the *dl*-1,2-dihydroxybutyric acid (m. p. 74°) has the same configuration as the racemic acid. It was thought necessary to complete this proof with the reactions of 3-bromothreonic acid, and the results of this investigation are reported in the present paper.

**I. Synthesis of 3-Bromothreonic Acid.**—The 3-bromothreonic acid is prepared by the oxidation of 3-bromocrotonic acid[3] with osmic acid activated barium chlorate in the same manner as was reported in the case of 3-chlorocrotonic acid.[2] The 3-bromothreonic acid hydrolyzes gradually in

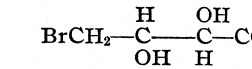
[1] Jeremiah Smith Fellow in Organic Chemistry from Hungary.

[2] Géza Braun, THIS JOURNAL, **52**, 3176 (1930).

[3] Géza Braun, *ibid.*, **52**, 3167 (1930).

aqueous solution; therefore care should be taken to protect it from the prolonged action of water. It is advisable to carry out the oxidation of 3-bromocrotonic acid in a minimum amount of water and, after the oxidation is completed, the 3-bromothreonic acid is best isolated by pouring the aqueous solution into a large amount of ether and then drying the solution completely with anhydrous sodium sulfate. The 3-bromothreonic acid is obtained then from the ethereal solution with 70% yield, whereas if the water is removed at reduced pressure in the usual manner, the yield is considerably lower.

According to analysis the hydroxylated product corresponds to a formula $C_4H_7O_4Br$. Its configuration was proved by conversion into racemic tartaric acid with dilute nitric acid. The acid can be directly oxidized with nitric acid; however, the oxidation is very slow and incomplete. It was found to be best to remove the bromine with silver acetate at first and then oxidize the resulting product with nitric acid. The oxidation yielded, except for a small amount of oxalic acid, exclusively racemic tartaric acid; therefore the compound has the same configuration as the racemic acid



*dl*-Threo-1,2-dihydroxy-3-bromobutyric acid or, briefly, 3-bromothreonic acid

The 3-bromothreonic acid has properties similar to those of 3-chlorothreonic acid, only its halogen is much more reactive, as would be expected. It precipitates sodium bromide from an acetone solution of sodium iodide and it seems to be converted into 3-iodothreonic acid by this process; but the crystalline 3-iodothreonic acid could not be isolated.

**II. Reduction of 3-Bromothreonic Acid.**—This was carried out in both acid and alkaline solutions, but it was possible to isolate the *dl*-1,2-dihydroxybutyric acid (m. p. 74°)—as a result of the reduction—only in alkaline solution. In acid solution there seems to be an hydrolysis rather than reduction, as for instance in case of reduction with zinc in 50% acetic acid the result of reduction is a lactone with a molecular weight of 118, which corresponds to the molecular weight of the lactone of threonic acid.

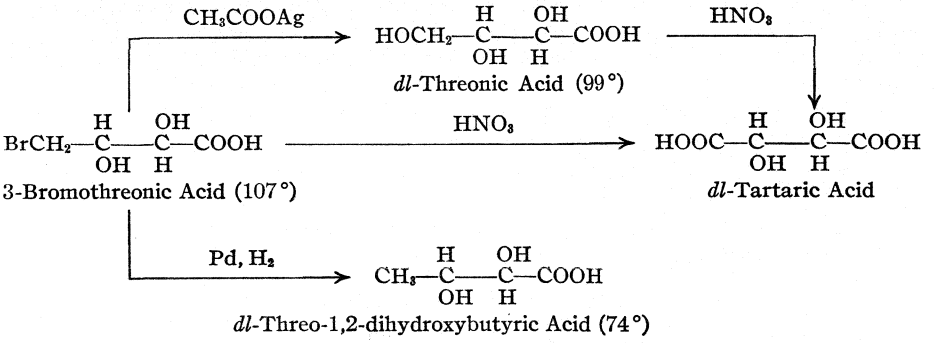
When the sodium 3-bromothreonate was reduced with palladium-activated hydrogen the reduction product showed some crystallization, after it was seeded with the crystals of *dl*-1,2-dihydroxybutyric acid (m. p. 74°), but no definite compound could be isolated. The sirupy acid according to titration had a molecular weight of 126. These experiments in acid solution show that the carboxyl group was not involved in the reduction.

The reduction of 3-bromothreonic acid in alkaline solution proceeds just as well as in the case of 3-chlorothreonic acid. The result of the reduction is the *dl*-1,2-dihydroxybutyric acid (m. p. 74°) with 70% yield.

**III. *dl*-Threonic Acid.**—The 3-bromothreonic acid is easily converted into *dl*-threonic (m. p. 98–99°) by treatment with silver acetate in aqueous

solution. This method, working in 10–20 g. lots, gives the threonic acid—also in the case of 3-chlorothreonic acid—in about 60% yield and is to be preferred to the previously published method through the barium salt with silver oxide.

A brief summary of the reactions carried out is given below




## Experimental Part

**3-Bromocrotonic acid (m. p. 74°)** was prepared from 2-hydroxy-3-bromo-*n*-butyronitrile as it was previously reported.[3]

**3-Bromothreonic Acid.**—Twenty-five grams of 3-bromocrotonic acid (m. p. 74°) was suspended (partially dissolved) in 200 cc. of ice water which contained 20 cc. of 1% osmic acid solution and 11 g. of barium chlorate and this solution was kept in ice water under frequent shaking. In about seven hours at 2–3° all of the acid went into solution, whereupon the reaction mixture was allowed to warm up to room temperature. The oxidation was complete in twenty hours; the acidity of the solution corresponded to 24.5 g. of 3-bromocrotonic acid. Then the osmic acid was extracted several times with benzene, the aqueous solution poured into 1.5 liters of ether and the mixture dried with anhydrous sodium sulfate (about 900 g.). After removal of solids the ethereal filtrate was completely dried and finally the pure ethereal solution concentrated to dryness at reduced pressure. The pale yellow residue, which soon solidified to a hard crystalline mass, weighed 26.5 g. or 85% of the theoretical. This was dissolved in a mixture of 20 cc. of ethyl acetate and 10 cc. of chloroform and cooled to −10°: 18.0 g. of crystals, m. p. 105°. The mother liquor gave in a similar manner 2.2 g. of crystals; the concentrated final mother liquor still deposited 0.8 g. of crystals overnight, making a total yield of 21.0 g., or 70% of the theoretical.

Recrystallization from 30 cc. of warm ethyl acetate and 10 cc. of warm chloroform yielded 17.0 g. of crystals (m. p. 107°) in ice.

*Titration.* Subs., 0.5626, 0.4432: 28.35, 22.30 cc. of 0.1 *N* alkali at room temp.; 28.35, 22.24 cc. of 0.1 *N* alkali and 28.1, 22.25 cc. of 0.1 *N* silver nitrate solution for organically bound bromine after saponification on the water-bath for fifteen minutes. Calcd. for $C_4H_7O_4Br$: mol. wt., 198.98; Br, 40.16. Found: mol. wt., 198.55, 198.7; Br, 39.92, 40.17.

*Anal.* Subs., 0.5626, 0.4432: AgBr, 0.5300, 0.4136. Calcd. for $C_4H_7O_4Br$: Br, 40.16. Found: Br, 40.09, 39.72.

### Oxidation of 3-Bromothreonic Acid with Nitric Acid

**(a) Direct Oxidation.**—One gram of 3-bromothreonic acid was dissolved in 20 cc. of nitric acid (sp. gr. 1.21) and heated for seventy-two hours at 56°, *i. e.*, until the evolu-

tion of brown gases ceased. The hydrogen bromide was precipitated with silver acetate (0.45 g. of silver bromide was obtained, about 25% of the theoretical) and then the nitric acid was removed at reduced pressure and the crystalline residue converted into potassium acid tartrate in the usual manner. Only 0.1 g. of potassium acid tartrate was isolated. This was recrystallized from water and titrated: 0.050 g. required 2.62 cc. of 0.1 *N* NaOH. Calcd. mol. wt. for $C_4H_5O_6K$: 188.1. Found: 190.1.

(b) Two grams of 3-bromothreonic acid was dissolved in 50 cc. of water and after addition of 4 g. of silver acetate the mixture was shaken at room temperature for about twenty hours. After removal of silver bromide (1.9 g.) and excess silver acetate, the pure filtrate was concentrated to dryness at reduced pressure and the residue oxidized with 10 cc. of nitric acid (sp. gr. 1.21) in the usual manner. The crystalline oxidized product gave 1.0 g. of recrystallized potassium acid tartrate (dried at 100°).

*Titration.* Subs., 0.5158: 27.2 cc. of 0.1 *N* of alkali. Calcd. mol. wt. for $C_4H_5O_6K$: 188.1. Found: mol. wt., 189.6.

The filtrate of potassium acid tartrate gave some calcium oxalate, but no mesotartaric acid was found.

### Reduction of 3-Bromothreonic Acid

(a) **With Zinc in Acetic Acid.**—Two grams of 3-bromothreonic acid was dissolved in 40 cc. of 50% acetic acid and under violent stirring 6 g. of zinc dust was added, in two lots, at 75°. In two and one-half hours the organic bromine was completely ionized, whereupon the hydrogen bromide was precipitated with a slight excess of silver acetate. Then the excess silver and zinc were precipitated with hydrogen sulfide and the filtrate of the sulfides was concentrated at reduced pressure. The residue was dissolved in water, concentrated again at reduced pressure and this operation repeated until the acetic acid was completely removed. The residue, 0.8 g. of pale yellow sirup, could not be crystallized.

*Titration.* Subs., 0.1700: 2.0 cc. of 0.1 *N* alkali at room temperature and 12.35 cc. of 0.1 *N* alkali after fifteen minutes' heating on the water-bath. Calcd. mol. wt. for threonic lactone, $C_4H_6O_4$: 118. Found: mol. wt., 118.4.

(b) **Reduction of 3-Bromothreonate.**—Two grams of 3-bromothreonic acid was dissolved in 40 cc. of water, the solution cooled in a freezing mixture until much ice appeared and then neutralized with 10 cc. of 1 *N* alkali. After addition of 5.0 g. of palladium-norit (corresponding to 0.25 g. of palladium), the mixture was shaken in a hydrogen atmosphere. The reduction proceeded rapidly at the beginning but soon stopped and started again only after neutralization of the acid formed. Altogether 225 cc. of hydrogen was consumed and 10 cc. of 1 *N* alkali used for neutralization. The solution was then filtered, and to the filtrate, which contained the theoretical amount of sodium bromide, 9 cc. of 1 *N* sulfuric acid was added and the reduction product isolated in the usual manner. About 1.0 g. of sirup was obtained, which showed some crystallization after it was seeded with the crystals of *dl*-1,2-dihydroxybutyric acid (m. p. 74°), but the amount of crystals was negligible.

*Titration.* Subs., 0.1700: 9.0 cc. of 0.1 *N* alkali at room temperature and 4.5 cc. after fifteen minutes' heating on the water-bath. Calcd. mol. wt. for dihydroxybutyric acid, $C_4H_8O_4$: 120. Found: mol. wt., 126.

(c) **Reduction in Alkaline Solution.**—Two grams of 3-bromothreonic acid was dissolved in 40 cc. of water, the solution cooled until much ice appeared and then 20 cc. of 1 *N* alkali and 5 g. of palladium-norit (0.25 g. of palladium) were added. Then the mixture was again cooled in ice and salt until almost solidified and was violently shaken in a hydrogen atmosphere, while the temperature was kept around 0° for about half an

hour. In about three hours 320 cc. of hydrogen was consumed and the reduction was complete.

After addition of 9 cc. of 1 *N* sulfuric acid the reaction mixture was worked up in the usual manner. There was obtained 0.85 g. of a pale yellow sirup (70% of the theoretical) which soon solidified to a hard crystalline mass. This gave 0.5 g. of crystals, m. p. 73–74°, from ethyl acetate. The mixed melting point with the *dl*-1,2-dihydroxybutyric acid (m. p. 74°) was 74°.

*Titration.* Subs., 0.1360: 11.02 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_4H_8O_4$: 120. Found: mol. wt., 123.

***dl*-Threonic Acid.**—Two grams of 3-bromothreonic acid was dissolved in 100 cc. of water and after addition of 4 g. of silver acetate the mixture was shaken at room temperature for fifteen hours. The reaction was complete by this time. To the filtrate of the silver salts 150 cc. of 0.2 *N* barium hydroxide was added and the silver oxide removed by filtration. Then the alkaline solution was heated at 75° for ten minutes and afterward allowed to stand overnight. From the filtrate of an unidentified barium salt the barium was quantitatively removed by sulfuric acid and then the clear filtrate concentrated at reduced pressure to a thick sirup. This was dissolved in a warm mixture of absolute alcohol and acetone, the clear solution poured off and concentrated at reduced pressure. The residue, about 1.1 g., soon solidified to a hard crystalline mass, which gave 0.3 g. of crystals, m. p. 99°, from acetone. A mixed melting point with *dl*-threonic acid of known purity (m. p. 98–99°) was 98–99°.

*Titration.* Subs., 0.1793: 13.00 cc. of 0.1 *N* alkali at room temperature and 0.07 cc. of 0.1 *N* alkali at 80°, total 13.07 cc. Calcd. for $C_4H_8O_5$: mol. wt., 136.06. Found: mol. wt. 137.1.

The author wishes to thank Dr. Arthur B. Lamb for the valuable suggestions during the course of the work, and gratefully acknowledges the financial support of Jeremiah Smith, donor of the Jeremiah Smith Fellowship, and the courtesies extended by Dr. C. N. Frey, Research Director of the Fleischmann Laboratories, which made this investigation possible.

## Summary

1. The oxidation of 3-bromocrotonic acid (m. p. 74°) with barium chlorate is reported. The oxidation yields the *dl*-threo-1,2-dihydroxy-3-bromobutyric acid (m. p. 107°) in 70% yield. The configuration of the hydroxylated product was proved by its conversion into racemic tartaric acid by direct and indirect oxidation with nitric acid.

2. Treatment of *dl*-threo-1,2-dihydroxy-3-bromobutyric acid with silver acetate gives the *dl*-threonic acid in good yield.

3. The reduction of *dl*-threo-1,2-dihydroxy-3-bromobutyric acid with palladium-activated hydrogen gives the *dl*-threo-1,2-dihydroxybutyric acid (m. p. 74°) in 70% yield.

These results confirm that the *dl*-1,2-dihydroxybutyric acid (m. p. 74°) has the same configuration as racemic tartaric acid and consequently the *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°) has a configuration corresponding to mesotartaric acid.

CAMBRIDGE, MASSACHUSETTS

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

# THE PREPARATION OF COPPER–CHROMIUM OXIDE CATALYSTS FOR HYDROGENATION

BY RALPH CONNOR, KARL FOLKERS AND HOMER ADKINS

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The copper–chromium oxide catalyst which recently has been found to be so effective in the hydrogenation of various organic compounds[1] in the liquid phase was originally prepared by the decomposition of a precipitated copper ammonium chromate. The process for the preparation of the catalyst was that used by Lazier[2] for the preparation of zinc and manganese "chromite" catalysts for the hydrogenation of carbon monoxide in the vapor phase.

The utilization of this catalyst soon raised a number of questions in regard to its preparation. In attempting to answer some of these questions a very considerable number of catalysts containing copper and chromium have been prepared by various procedures. In order to bring some semblance of order into the presentation of a rather empirical investigation the modifications in the ingredients and procedures for the preparation of catalysts will be considered under three heads: (1) the improvement of the method for the preparation of a catalyst through the decomposition of copper ammonium chromate; (2) the promotion and stabilization of the activity of copper chromium oxide catalysts by the addition of another metal to the catalyst; (3) the development of methods, other than the decomposition of the chromates, for the preparation of copper–chromium oxide catalysts.

**Testing the Activity of Catalysts.**—The copper–chromium oxide catalysts described in this paper were tested under arbitrarily chosen conditions and they are compared on the basis of the results obtained. It is realized fully that if the catalyst had been tested in the hydrogenation of other compounds under different conditions of temperature, pressure, ratio of catalyst, etc., the relative merits of the catalyst might have been different. It was recently pointed out[3] that even the relative activity of two preparations of catalyst was a function of the particular set of experimental conditions (hydrogen acceptor, temperature, hydrogen pressure, amount of catalyst, ratio of catalyst to hydrogen acceptor, thoroughness of dispersion of catalyst in reaction mixture, etc.) used in testing the activity. It was also indicated that catalysts for hydrogenation

[1] Adkins, Connor and Folkers, THIS JOURNAL, **53**, 1091, 1095 (1931).

[2] Lazier, British Patent 301,806, January 12, 1926; U. S. Patent 1,746,783, February 11, 1930.

[3] Adkins and Covert, *J. Phys. Chem.*, **35**, 1684 (1931).

may have several different characteristics any one of which may serve as a basis of comparison.

Acetone, furfural, ethyl β-phenylpropionate, ethyl phenylacetate, ethyl hexahydrobenzoate and spermaceti (*i. e.*, crude cetyl palmitate) have been used to test the activity of these catalysts. These compounds were selected on the basis of the following considerations. Acetone is very readily hydrogenated, so it is a suitable compound for testing rather inactive catalysts. If a catalyst will not induce the hydrogenation of acetone, it is indeed a poor catalyst. If a catalyst was found to be rather inactive toward acetone it was not in general tested against the more difficultly hydrogenated compounds. Furfural is not so readily hydrogenated as acetone, and so it imposes a more severe test on a catalyst. The hydrogenation of the esters to the corresponding alcohols involves a hydrogenation distinctly different from that in the hydrogenation of aldehydes and ketones and requires a much higher temperature and a more stable catalyst. β-Phenylpropionic and hexahydrobenzoic esters and spermaceti were selected because of their availability and because their hydrogenation is typical of a large number of esters. Phenylacetic ester was used because it offers further complications in that the alcohol (β-phenylethyl) is readily hydrogenated to ethylbenzene.

**Activity of Catalysts from Copper Ammonium Chromate.**—The procedure for the preparation of a catalyst by the decomposition of an ammonium chromate given for catalysts 25 and 36 KAF and 28 RAC is one which was gradually developed in this Laboratory. It has been repeated many times and has been found to give uniformly excellent results.

**Preparation of Catalysts from Copper-Barium-Ammonium Chromates (25,36 KAF, 28 RAC).**—Nine hundred ml. of a solution (80°) containing 261 g. of hydrated copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) and 31.3 g. of barium nitrate was added to 720 ml. of a solution (25–30°) containing 151.2 g. of ammonium dichromate and 150 ml. of 28% ammonium hydroxide. The precipitate was filtered, the cake being pressed with a spatula and sucked as dry as possible. After drying in an oven at 75–80° overnight, and pulverizing, the product weighed 234 g. It was decomposed in three portions in a casserole over a free flame. In carrying out the decomposition, the powder was stirred with a spatula from the beginning of the heating, and the flame was removed after the decomposition was well started. After a little more stirring, there was a sudden evolution of gases and the entire mass became black. After another thorough stirring the powder was removed from the hot casserole and allowed to cool. The combined product was then leached for thirty minutes with 600 ml. of 10% acetic acid solution, filtered, and washed with 600 ml. of water in six portions, dried overnight at 125°, and pulverized. The product weighed 149.5 g.

The activity of the catalysts so prepared is evidenced by the fact that 3 g. of catalyst No. 25 KAF induced rather rapid hydrogenation of 75 g. of furfural under a pressure of 163 ± 27 atmospheres of hydrogen, at a temperature of 130–135°. The furfural was completely hydrogenated to tetrahydrofurfuryl alcohol within about ten minutes as the bomb was heated up to 160–165°. The hydrogenation was complete within four minutes after the temperature of the bomb reached 160°. Five grams of this catalyst brought about the complete hydrogenation of 0.25 mole of ethyl hexahydrobenzoate at 250° within fifty-two minutes. Further washing of the catalyst with 20% acetic acid enhanced its activity so that the time required for the hydrogenation of the ester was reduced to thirty minutes. Heating the catalyst to 400° for two minutes did not decrease its activity.

Both the amount and activity of the catalyst obtained in a given preparation were found to vary with the quantity of ammonium hydroxide used for the precipitation of the copper ammonium chromate. A series of catalysts (31, 32, 33 and 34 KAF) were made on one-third the scale of No. 25 KAF, in which the amount of ammonium hydroxide used was variously 125, 75, 50 and 20 ml. When these catalysts were tested on furfural, under the conditions noted above, 101, 0.5, 23 and 45 minutes were required for complete hydrogenation after the temperature of the bomb reached 160°. The proportion of ammonium hydroxide used in preparing catalyst No. 32 KAF was the most advantageous not only because it gave the most active catalyst but also because it gave a considerably larger yield of catalyst. In washing this series of catalysts a 40% solution of acetic acid was tried instead of the 10% solution used in the procedure for catalyst 25 KAF. This more drastic washing of the catalyst was quite satisfactory in the smaller scale of operation used in preparing catalysts 31, 32, 33 and 34 KAF but when it was used on the triple scale of 35 KAF a rather poor catalyst was obtained. The procedure given for catalyst No. 37 KAF is a combination of the procedures for 25 and 32 KAF and represents the best method so far found for the preparation of a copper–chromium–barium oxide catalyst. When this catalyst was tested on furfural, as described above, hydrogenation was complete in two minutes after the temperature of the bomb reached 160°.

Catalyst 37 KAF was prepared as follows. Nine hundred ml. of a solution (80°) containing 261 g. of hydrated copper nitrate and 31.3 g. of barium nitrate was added to 900 ml. of a solution (25–30°) containing 151.2 g. of ammonium dichromate and 225 ml. of 28% ammonium hydroxide. The procedure from this point was the same as that given for 25 KAF. The yield of catalyst was 170 g.

Catalysts which contained cadmium (27 KAF) or silver (30 KAF) in addition to copper, barium and chromium were not particularly active.

Ethyl hexahydrobenzoate (0.25 mole) with 5 g. of catalyst was completely reduced at 250° within 210 minutes by 27 KAF and in 113 minutes by 30 KAF. The former catalyst was made through the precipitation of the carbonate with sodium bicarbonate while the latter was made by the dichromate method.

**The Stabilization and Promotion of the Activity of Copper–Chromium Oxide Catalysts.**—The active catalysts containing copper which have been used in this Laboratory are all black or dark brown in color and apparently contain the copper in the divalent state. These dark colored catalysts are under some conditions reduced to reddish colored compounds. This reduction of the copper from the divalent to the monovalent or elementary state occurs for example at 360° when ethanol is passed over the catalyst. The reduction also occurs in the presence of certain more easily oxidized compounds at temperatures as low as 150 to 175°. The resulting reddish copper compound is rather inactive for hydrogenation although it has a high catalytic activity for some other types of reaction as, for example, the conversion of aldehydes into esters.

It has been found advantageous to have barium,[4] calcium or magnesium compounds present in the copper–chromium oxide catalyst in order to retard or inhibit reduction of the catalyst. For example, two samples of catalyst prepared in the same way, but one containing only copper and chromium (20 RAC) and the other containing barium, copper and chromium (22 RAC), were tested against ethyl caprylate. The one containing barium induced 90% hydrogenation of the ester after 7.25 hours and was black in color when it was removed from the reaction mixture. The catalyst which contained no barium failed to bring about any appreciable hydrogenation of the ester and was bright red in color when it was removed from the ester. These two catalysts showed very little difference in the rate at which they catalyzed the hydrogenation of acetone and furfural; thus it appears that the effect in the case of the ester was not so much to promote the activity of the catalyst as it was to stabilize it against reduction.

The necessity for the incorporation of barium, calcium or magnesium in the catalyst varies with the ester and with its purity, and also with the proportion of ester to catalyst used. If a high ratio of a very active catalyst is used, then the hydrogenation may be complete before the catalyst is reduced.

The effect of the presence of calcium as a component of the catalyst is indicated by the results obtained in the hydrogenation of ethyl α-phenylbutyrate. Under identical conditions a catalyst (18 KAF) containing only copper and chromium required 36 minutes for the hydrogenation of this ester, while a catalyst (39 KAF) which contained calcium

[4] *Cf.* Connor, Folkers and Adkins, THIS JOURNAL, **53**, 2012 (1931).

brought about the hydrogenation in five minutes. The ratio of the products was almost the same, *i. e.*, 1 to 3% residual ester, 15 to 19% hydrocarbons and 78 to 79% 2-phenylbutanol-1. The addition of magnesium or calcium to a copper–chromium oxide reduced the time for the hydrogenation of ethyl phenylacetate to approximately 35% of that required by the simpler catalyst. The introduction of an additional component to the copper–chromium oxide catalyst not only appears to stabilize the catalyst against reduction and to enhance the activity but also modifies the ratio of the product formed in the hydrogenation of such a compound as ethyl phenylacetate. The ratio of ethylbenzene to phenylethyl alcohol for calcium being 1 to 6 and for magnesium 1 to 2. The complete data in support of these statements is given in Table I of the accompanying paper on hydrogenation of esters.

**Preparation of Catalysts Containing Magnesium, Calcium and Strontium.**—Catalysts 38, 39 and 40 KAF containing magnesium, calcium and strontium, respectively, were prepared on one-third the scale but in the same manner as 25 KAF, except that 10.3 g. of magnesium nitrate hexahydrate, 6.6 g. of calcium nitrate or 8.5 g. of strontium nitrate was substituted for the barium nitrate. The weights of product were 34, 38 and 36 g., respectively.

**The Preparation of Copper Oxide Catalysts Other than Through the Decomposition of the Chromates.**—Data on the activity of eighteen catalysts prepared otherwise than by the decomposition of copper ammonium chromate have been summarized in Table I. It is apparent that all the products which contained divalent copper catalyzed hydrogenation, while the one which contained cuprous copper was inactive. Cupric oxide alone (14 RAC—prepared by decomposition of copper oxalate) catalyzed the hydrogenation of acetone, but a temperature of 200° was necessary for very rapid hydrogenation and the catalyst was in the red form after the run. The presence of chromium oxide (21 RAC—prepared by mixing the copper oxalate with ammonium dichromate before the decomposition) caused the hydrogenation of acetone as rapidly at 150° as the copper oxide had done alone at 200°. This catalyst was black after the run. The desirability of mixing the components before decomposition is shown by a comparison of catalysts 21 RAC and 33 RAC made by the same procedure except that in one case the copper oxalate and ammonium chromate were mixed before decomposition, and in the other these components were decomposed separately and then mixed. The latter method gave a much inferior catalyst.

Copper oxide (Mallinckrodt's) was superior to that prepared from the oxalate (33 RAC and 26 RAC). It seemed to make no difference, however, whether commercial $Cr_2O_3$ was used or whether this oxide was prepared by decomposition of ammonium dichromate (23 RAC and 26 RAC; 23a RAC and 26a RAC).

TABLE I

CATALYTIC ACTIVITY OF VARIOUS COPPER OXIDE CATALYSTS AT 150–250 ATMOSPHERES

| Source of catalyst[e] | Catalyst No. | Acetone[a] | Furfural[b] | Esters |
|---|---|---|---|---|
| Copper oxalate | 14 RAC | 14 m. (200°) | | |
| CuO *ex* oxalate + $Cr_2O_3$ *ex* $(NH_4)_2Cr_2O_7$ | 33 RAC | 300 m. (175°) | | |
| Copper oxalate + $(NH_4)_2Cr_2O_7$ | 21 RAC | 13 m. (150°) | | |
| Copper oxalate + $(NH_4)_2Cr_2O_7$ + $BaCrO_4$ | 27 RAC | | | 50% (10.5 hrs.)[c] |
| Cu, Cr, Ba oxalates (coppt.) | 25 RAC | | 20 m. (160°) | 66% (11.5 hrs.)[c] |
| Mixture of CuO + $Cr_2O_3$ | 23 RAC | 75 m. (175°) | | |
| Mixture of CuO + $Cr_2O_3$ (5 m. at 450°) | 23a RAC | 30 m. (175°) | | |
| Mixture of CuO + $Cr_2O_3$ *ex* $(NH_4)_2Cr_2O_7$ | 26 RAC | 70 m. (175°) | | |
| Mixture of CuO + $Cr_2O_3$ *ex* $(NH_4)_2Cr_2O_7$ (5 m. at 450°) | 26a RAC | 20 m. (175°) | | |
| Mixture of CuO + $Cr_2O_3$ *ex* $(NH_4)_2Cr_2O_7$ (1 hr. at 450°) | 26b RAC | 45 m. (175°) | | |
| Mixture of CuO with BaO and $Cr_2O_3$ *ex* $BaCrO_4$ and $(NH_4)_2Cr_2O_7$ | 32 RAC | | | 85% (7.2 hrs.)[d] |
| CuO + $BaCrO_4$ + $(NH_4)_2Cr_2O_7$ | 24 RAC | | 120 m. (160°)<br>50 m. (175°) | 85% (12 hrs.)[c] |
| Cu, Cr, $NH_4$ carbonates (coppt.) | 20 RAC | 12 m. (150°) | 80 m. (160°) | |
| Cu, Cr, Ba, $NH_4$ carbonates (coppt.) (0.5 as much Cu as 30 RAC) | 22 RAC | 11 m. (150°) | 90 m. (160°) | 36% (11 hrs.)[c] |
| Cu, Cr, Ba, $NH_4$ carbonates (coppt.) | 30 RAC | | 5 m. (160°) | 100% (2 hrs.)[d] |
| Cu, Cr, Ba nitrates | 31 RAC | 20 m. (150°) | 105 m. (160°) | 100% (3.5 hrs.)[d] |
| Cu + $CrO_3$ | 34 RAC | | 175 m. (160°) | |
| $Cu_2O$ + $Cr_2O_3$ | 35 RAC | No activity (200°) | | |

[a] 58 g. acetone, 1.9 g. of catalyst. [b] 75 g. furfural, 3.0 g. of catalyst. [c] 75 g. of spermaceti, 5 g. of catalyst at 250°. [d] 30 g. of ethyl β-phenylpropionate, 4 g. of catalyst at 250°. [e] A detailed description of the preparation of all of these catalysts was given in the original manuscript submitted to the Editor but due to the necessity for the economy of space these descriptions have been eliminated from the published paper. The catalysts *ex* oxalates, dichromates, carbonates and nitrates were prepared by the decomposition of these salts in the manner described in detail for catalysts 25 KAF and 30 RAC. The preparation of oxide catalysts by the decomposition of oxalates was patented by Lazier (U. S. Patent 1,746,781, February 11, 1930). However, the method was used in this Laboratory for the preparation of copper oxide some years earlier [Adkins and Lazier, THIS JOURNAL, **46**, 2295 (1924)].

The catalyst (30 RAC), made by coprecipitation of copper, barium and chromium carbonates, is very distinctly superior to the other catalysts listed in Table II, and is similar in activity to the better catalysts from the chromate. Aside from pointing out the distinct superiority of the carbonate catalysts over the others listed in Table II, it is not felt that the data at hand is sufficient to warrant a decision as to the relative activities of catalysts resulting from other methods of preparations. A change in the quantities of materials used, variations in technique (such as thoroughness of mixing or drying), etc., may cause a marked difference in the activity of the product. It is quite likely that all of the procedures used in the preparation of these catalysts could be modified so as to give more active catalysts. An extensive and precise comparison of the various procedures for the preparation of copper–chromium oxide catalysts is beyond the scope of this work. The salient conclusion that emerges from the data in Table I is that copper–chromium oxide catalysts active for hydrogenation may be prepared by numerous and varied ways, with or without coprecipitation. Even the simplest catalyst—made by grinding together the oxides of copper, chromium and barium and heating them at 450° for five minutes (32 RAC)—catalyzed the hydrogenation of ethyl β-phenylpropionate to γ-phenylpropanol.

**Preparation of a Catalyst (30 RAC) from Copper-Barium-Ammonium Carbonates.**—Solutions of the three metallic nitrates were prepared separately as follows: 5.4 g. of barium nitrate ($Ba(NO_3)_2$) in 50 ml. of boiling water, 77.2 g. of hydrate of chromium nitrate ($Cr_2(NO_3)_6 \cdot 15H_2O$) in 450 ml. of warm water, 100 g. of hydrated copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) in 150 ml. of water. The three solutions were mixed (35°) and 94.4 g. of ammonium carbonate ($(NH_4)_2CO_3 \cdot H_2O$) in 535 ml. of water was added. There was a considerable amount of effervescence and a very voluminous precipitate was formed. The precipitate was filtered with suction, washed twice with 50 ml. portions of water, dried at 110–120°, pulverized and decomposed in two portions at 190–230°. The product was then suspended in 100 ml. of a 10% solution of acetic acid, filtered, washed with two 75 ml. portions of water and dried at 110–120°. The product weighed 57 g.

## Summary

The procedure for the preparation of copper–chromium oxide catalysts by the precipitation and decomposition of copper ammonium chromate has been modified and improved so that much larger yields of a considerably more active catalyst may now be obtained.

It has been shown to be advantageous to incorporate barium, calcium or magnesium into the copper–chromium oxide catalyst. The addition of one of these elements stabilizes the catalyst against reduction and consequent deactivation and apparently enhances its activity. These elements also

modify the relative rates of competitive hydrogenations such as are encountered in the preparation of phenylethyl alcohol from ethyl phenylacetate so that larger yields of the alcohols were obtained. The procedure for the preparation of the most active catalysts containing barium is that described for the catalyst labeled 37 KAF, while the most active catalyst yet prepared is that containing calcium and is labeled 39 KAF.

Copper–chromium oxide catalysts have also been prepared by the decomposition of oxalates, by the mechanical mixture of copper and chromium oxides, by the decomposition of their nitrates, by the combination of copper and chromic oxide and by the decomposition of the precipitated copper, chromium, ammonium carbonates. All the products which contained divalent copper catalyzed hydrogenation. The most active catalysts (30 RAC) from this group were prepared by the decomposition of coprecipitated copper, chromium, barium, ammonium carbonates. Such a catalyst was similar in activity to the better catalysts obtained by the decomposition of the corresponding chromates.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# THE CATALYTIC HYDROGENATION OF ESTERS TO ALCOHOLS. II

BY KARL FOLKERS AND HOMER ADKINS

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The catalytic hydrogenation over copper–chromium oxide of the carbethoxy to the carbinol group in 80–98% yields for seven esters was recently described.[1] Because of the utility of this process for the reduction of an ester to the corresponding alcohol, several of the variables involved have been studied further, and the method has been extended to other types of esters, over modified and improved copper–chromium oxide catalysts. This paper, then, is a summary of the significant results of all these experiments. The apparatus and procedure were the same as those previously described.[2]

In Table I there is recorded a summary of the data obtained on the hydrogenation of various esters at 250° and under a pressure of 200 to 300 atmospheres. Table II contains the data on the rates of hydrogenation of

[1] Adkins and Folkers, THIS JOURNAL, **53**, 1095 (1931). Since the publication of this paper and the completion of most of the experimental work described herewith, there have appeared three publications describing the hydrogenation of a few acids and esters of high molecular weight to alcohols. Schrauth, Schenck and Steckdorn, *Ber.*, **64**, 1314 (1931); Norman, *Z. angew. Chem.*, **44**, 714 (1931); Otto Schmidt, *Ber.*, **64**, 2051 (1931).

[2] Adkins and Cramer, THIS JOURNAL, **52**, 4349 (1930).

eight caproic esters as determined at 225° and under a pressure of 177 ± 13 atmospheres of hydrogen, using 2 g. of copper–barium–chromium oxide These conditions were selected so that differences in the rates of hydrogena-

TABLE I

HYDROGENATION OF ESTERS (250°) (200–300 ATMOSPHERES)

| Ester Name | Ester Mole | Catalyst Oxides | Catalyst g. | Catalyst No. | Time, hours | Yields, % | Products |
|---|---|---|---|---|---|---|---|
| Methyl caproate[a] | 0.20 | Cu Ba Cr | 5 | 19 | 2.25 | 92.2 | *n*-Hexanol (152–153°) |
| *n*-Butyl caproate[a] | .20 | Cu Ba Cr | 5 | 19 | 0.58 | 95.5 | *n*-Hexanol (152–153°) |
| Ethyl caprylate | .20 | Cu Ba Cr | 5 | 19 | 2.0 | 93.6 | *n*-Octanol (189–190°) |
| Methyl salicylate | .25 | Cu Cr | 6 | 18 | 6.0 | 19.2 | *o*-Cresol (182–185°) |
| | | | | | | 61.3 | 2-Methyl cyclohexanol (161–162°) |
| Ethyl hexahydrobenzoate | .25 | Cu Ba Cr | 5 | 25 | 0.87 | 97.5 | Cyclohexylcarbinol (180–181°) |
| Ethyl hexahydrobenzoate | 1.78 | Cu Ba Cr | 10 | 20 | 3.5 | 97.5 | Cyclohexylcarbinol |
| Diethyl malonate | 0.20 | Cu Ba Cr | 6 | 20 | 7.5 | ... | Ethyl propionate, *n*-propanol |
| Diethyl ethylmalonate | .20 | Cu Ba Cr | 5 | 25 | 2.0 | 77.9 | 2-Methylbutanol-1 (ester free) (120–124°) |
| Diethyl ethylmalonate | .27 | Cu Ba Cr | 6 | 25 | 0.5 | 71.9 | 2-Methylbutanol-1 (120–124°) |
| | | | | | | 19.3 | Ethyl 2-methylbutyrate |
| | | | | | | 8.8 | Diethyl ethylmalonate |
| Dimethyl α-phenylsuccinate<br>Methanol | .23<br>.87 | Cu Ba Cr | 8 | 24 | 1.5 | 100 | Dimethyl α-phenylsuccinate |
| Dimethyl α-phenylsuccinate[i] | .23 | Cu Ba Cr | 6 | 24 | 6.0 | 67.3 | 3-Phenylbutanol-1 (92–94°) |
| | | | | | | 12.6 | 2-Phenylbutanediol-1,4 |
| | | | | | | 1.2 | Dimethyl α-phenylsuccinate |
| Ethyl β-phenylpropionate[m] | .17 | Cu Ba Cr | 4 | 20 | 1.0 | 93.0 | 3 - Phenylpropanol - 1 122–125° (19 mm.) |
| Di-*n*-butyl glutarate | .20 | Cu Ba Cr | 7 | 24 | 1.83 | 92.2 | Pentanediol-1,5 (108–110, 2.5 mm.) |
| Diethyl sebacate | .12 | Cu Ba Cr | 5 | 20 | 1.66 | 94.0 | Decanediol-1, 10 (150–151, 3 mm.) (m. p. 70.8–71.8°) |
| Ethyl lactate[b] | .26 | Cu Ba Cr | 5 | 25 | 4.42 | 83.5 | Propanediol-1,2 (186.5–187) (ester free) |
| Ethyl lactate[b] | .26 | Cu Ba Cr | 5 | 25 | 3.5 | 90.5 | Propanediol-1,2 (186.5–187) |
| | | | | | | 0.5 | Ethyl lactate |
| Ethyl β-hydroxybutyrate | .30 | Cu Ba Cr | 6 | 19 | 5.0 | 55.5 | Pri. and *sec.*-butanols |
| Ethyl β-acetyloxybutyrate | .19 | Cu Ba Cr | 5 | 24 | 4.0 | ... | Ethyl, pri. and *sec.*-butanols and their acetic and butyric esters |
| γ-Valerolactone | .28 | Cu Ba Cr | 5 | 24 | 0.0 | 78.5 | Pentanediol-1,4 (114–115, 8 mm.) |
| | | | | | | 8.1 | *n*-Pentanol |
| Caproic acid<br>*n*-Butanol[c] | .26<br>1.16 | Cu Ba Cr | 6 | 20 | 3.25 | 14.7 | *n*-Hexanol (152–153°); recovered acid (95.5% as ester, 4.5% as free acid) |
| Caproic acid<br>Ethanol[c] | 0.26<br>1.16 | Cu Ba Cr | 6 | 20 | 3.0 | 10.0 | *n*-Hexanol (152–153)°; recovered acid (93.8% as ester, 6.2% as free acid) |
| Stearic acid<br>*n*-Butyl stearate<br>*n*-Butanol | 0.056<br>.144<br>.54 | Cu Ba Cr | 8 | 24 | 11.0 | 77.1 | Octadecanol |
| Spermaceti[m] | .15 | Cu Ba Cr | 5 | 25 | 2.0 | 97 | Cetyl alcohol (ester free) |

TABLE I (*Concluded*)

| Ester: Name | Ester: Mole | Catalyst: Oxides | Catalyst: g. | Catalyst: No. | Time, hours | Yields, % | Products |
|---|---|---|---|---|---|---|---|
| Ethyl β-piperidino-propionate | .29 | Cu Ba Cr | 8 | 24 | 10.75 | ... | Piperidine; N-ethyl and propylpiperidines; ethyl propionate γ-piperidino-propanol; residue |
| Ethyl nicotinate<br>Ethanol | .22<br>1.08 | 0.6 g. reduced Ni on 3.4 g. kiselguhr (165°) | | | 3.25 | 72.6<br>27.0 | Ethyl nipecotate (78.7–79.5, 5 mm.); 3-Methyl piperidone-2[j] (102–102.5, 3 mm.) m. p. 54.5–56.5) |
| N-capropylpiperidine | .12 | Cu Ba Cr | 2 | 25 | 5.0 | 92.3 | N - *n* - hexylpiperidine (212–213°) |
| Ethyl nicotinate<br>Ethanol | .175<br>.874 | 0.75 g. reduced Ni on 4.25 g. kieselguhr (200°) | | | 7.0 | 68.0 | Ethyl N-ethyl nipecotate (80.5–82 (4 mm.)) |
| Ethyl N-ethylnipecotate | .13 | Cu Ba Cr | 3 | 37 | 2.2 | 99.0 | N - ethyl - β - pipecoline (142–144°) |
| Ethyl nicotinate | .22 | Cu Ba Cr | 6 | 25 | 7.0 | ... | Alkyl piperidines, ethyl nipecotate, cleavage and condensation products |
| Ethyl α-phenylbutyrate[d,k] (81–83° (4 mm.)) | .25 | Cu Cr | 6 | 18 | 7.0 | 0.0<br>48.0<br>47.5 | Ethyl α-phenylbutyrate<br>Hydrocarbons [l]<br>β-Ethylphenethyl alcohol (234–236°) |
| Ethyl α-phenylbutyrate[d] | .25 | Cu Cr | 6 | 18 | 0.58 | 3.2<br>14.6<br>78.1 | Ethyl α-phenylbutyrate<br>Hydrocarbons [l]<br>β-Ethylphenethyl alcohol |
| Ethyl α-phenylbutyrate[d] | .25 | Cu Cr | 6 | 18 | 0.05 | 24.0<br>9.3<br>63.5 | Ethyl α-phenylbutyrate<br>Hydrocarbons [l]<br>β-Ethylphenethyl alcohol |
| Ethyl α-phenylbutyrate[d] | .25 | Cu Ca Cr | 6 | 39 | 0.08 | 1.3<br>19.4<br>79.2 | Ethyl α-phenylbutyrate<br>Hydrocarbons [l]<br>β-Ethylphenethyl alcohol |
| Ethyl phenylacetate[e] | .25 | Cu Ba Cr | 6 | 25 | 0.85 | 1.3<br>52.5<br>39.7 | Ethyl phenylacetate<br>Ethylbenzene<br>Phenylethyl alcohol |
| Cyclohexyl phenylacetate[e] (129–130.5° (3.5 mm.)) | .25 | Cu Ba Cr | 6 | 25 | 0.53 | 5.9<br>35.4<br>58.7 | Ethyl phenylacetate<br>Ethylbenzene<br>Phenylethyl alcohol |
| Cyclohexyl phenylacetate[e] | .25 | Cu Ca Cr | 6 | 39 | 0.53 | 10.2<br>26.4<br>63.3 | Cyclohexyl phenylacetate<br>Ethylbenzene<br>Phenylethyl alcohol |
| Ethyl phenylacetate[f] | .28 | Cu Ba Cr | 2.5 | 25 | 5.0 | 0.0<br>69.7<br>20.3 | Ethyl phenylacetate<br>Ethylbenzene<br>Phenylethyl alcohol |
| Ethyl phenylacetate[f] | .28 | Cu Mg Cr | 2.5 | 38 | 1.78 | 7.5<br>30.6<br>58.3 | Ethyl phenylacetate<br>Ethylbenzene<br>Phenylethyl alcohol |
| Ethyl phenylacetate[f] | .28 | Cu Ca Cr | 2.5 | 39 | 0.42 | 37.8<br>8.4<br>50.7 | Ethyl phenylacetate<br>Ethylbenzene<br>Phenylethyl alcohol |
| Ethyl phenylacetate[f] | .28 | Cu Sr Cr | 2.5 | 40 | 1.6 | 90.1<br>...<br>2.9 | Ethyl phenylacetate<br>Ethylbenzene<br>Phenylethyl alcohol |
| Ethyl phenylacetate[g] | .20 | Cu Cr | 5 | 18 | 1.0 | 0.0<br>88.7<br>4.5 | Ethyl phenylacetate<br>Ethylbenzene<br>Phenylethyl alcohol |
| Ethyl phenylacetate[g] | .20 | Cu Ba Cr | 5 | 29 | 1.0 | 0.0<br>66.0<br>29.9 | Ethyl phenylacetate<br>Ethylbenzene<br>Ethyl phenyl alcohol |

*a, b, c, d, e, f, g, h.* Experiments bearing the same letter were carried out under identical conditions with the same sample of ester, etc.

[i] This ester was supplied by Dr. C. F. H. Allen of McGill University, Montreal.

[j] M. p. 53.5–55° [Aschan, *Ber.*, **24**, 2445 (1891)]; m. p. 55–56° [Lipp and Widnmann, *Ann.*, **409**, 144 (1915)].

[k] This ester was supplied by Dr. V. H. Wallingford of the Mallinckrodt Chemical Works, St. Louis.

[l] Apparently a certain amount of cleavage had occurred as the mixture of hydrocarbons distilled from 135 to 170°, and appeared to be a mixture of ethyl and secondary butylbenzenes boiling chiefly at 138–140 and 169–170°, respectively.

[m] These esters were hydrogenated by Mr. Ralph Connor.

TABLE II

RATE OF HYDROGENATION OF CAPROIC ESTERS (225°) (177 ± 13 ATMOSPHERES)

| Ester (0.12 mole) | Hydrogenation after 1.5 hrs., % | Total time, hrs. | Products: *n*-Hexanol | Products: Ester |
|---|---|---|---|---|
| Ethyl caproate | 44.7 | 7.5 | 62.4 | 37.6 |
| *n*-Butyl caproate | 57.7 | 6.25 | 85.0 | 15.0 |
| *n*-Butyl caproate, methanol | 42.1 | 7.5 | 89.4 | 10.6 |
| *Sec.*-butyl caproate | 58.6 | 8.0 | 82.8 | 17.2 |
| β-Ethoxyethyl caproate, 74–76° (2 mm.) | 60.1 | 6.84 | 90.9 | 9.1 |
| *n*-Hexyl caproate, 84–86° (3 mm.) | 65.2 | 7.64 | 96.3 | 3.7 |
| Cyclohexyl caproate, 116–117° (11 mm.) | 91.6 | 3.0 | 100.0 | 0.0 |
| Hexahydrobenzyl caproate, 100–102° (2 mm.) | 68.2 | 10.41 | 94.7 | 5.3 |
| Lauryl caproate, 148–149° (2 mm.) | 43.8 | 8.66 | 68.9 | 31.1 |

tion of the esters would be more marked than they are at higher temperatures. The hydrogenation of any of these caproates could have been easily made 100% by a slight increase of temperature, pressure or ratio of catalyst to ester. The yields of the major products given are those actually obtained by fractional distillation through Widmer columns, while the minor products were determined by titration, saponification, etc., of small samples. The preparation of the catalysts is described in the accompanying paper.[3]

## Discussion of Experimental Results

It is unnecessary to make any extended comment upon the hydrogenation of ethyl hexahydrobenzoate, caproate, caprylate, β-phenyl propionate, stearate, palmitate, glutarate and sebacate for these esters, like those of valeric, trimethylacetic, myristic and lauric acids reported in the earlier paper, were hydrogenated smoothly and almost quantitatively to the corresponding alcohols. However, the hydrogenation of esters is somewhat modified if there are certain groups or linkages in the vicinity of the carbethoxy group. Among these active substituents are the phenyl, hydroxyl, carbethoxy and amino groups. The hydrogenation is also modified by a number of other factors which are discussed below.

**Phenyl Group.**—Benzyl alcohol, phenylmethylcarbinol and diphenylcarbinol were readily hydrogenated over copper–chromium oxide catalysts

[3] Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

to the corresponding hydrocarbons at temperatures 50 to 100° lower than are necessary for the hydrogenation of esters.[4] It thus appeared hopeless to attempt to hydrogenate, to the corresponding phenylcarbinols, esters having a carbethoxy group attached to a benzenoid ring. This expectation was borne out by the absence of *o*-hydroxybenzyl alcohol in the products from the hydrogenation of methyl salicylate.

A similar hydrogenation to a hydrocarbon (ethylbenzene) was encountered in the earlier experiments on the hydrogenation of ethyl α-phenylacetate. However, it was found that if the hydrogenation was stopped before the absorption of hydrogen was complete, a 39.7% yield of β-phenylethyl alcohol could be obtained. The yield of ethylbenzene in this case was 52.5% of the theoretical amount. It thus appears that if the phenyl group is one carbon removed from the carbethoxy (or the resulting carbinol group), it is far less effective in labilizing the oxygen than it is when it is directly attached to the carbethoxy or carbinol group. This is further evidenced by the results of the hydrogenation of α-phenylbutyric ester. Under favorable conditions this compound was hydrogenated to give a 78% yield of 2-phenylbutanol-1 (β-ethylphenethyl alcohol), with only a 14.6% yield of hydrocarbons. The better yield of alcohol from α-phenylbutyric ester as compared with the yield from α-phenylacetic ester is apparently dependent upon the more rapid hydrogenation of the former ester. The more rapid hydrogenation of the ester makes it unnecessary to expose the alcohol so long to the conditions which convert it to a hydrocarbon.

The yield of phenylethyl alcohol from the esters of phenylacetic acid may be materially increased over the figure given (39.7%) above as the maximum so far obtained from the ethyl ester over a copper–barium–chromium oxide catalyst. For example, the actual yield of phenylethyl alcohol from the cyclohexyl ester was 58.7% over a barium containing catalyst and 63.3% over a catalyst containing calcium. These yields were 62 and 70%, respectively, based upon the amount of ester undergoing hydrogenation. In another experiment with a calcium-containing catalyst the yield of the alcohol, based upon the amount of ester hydrogenated, was approximately 80%.

The removal of the phenyl group one position further from the carbethoxy (or carbinol) group, as in β-phenylpropionic ester, almost eliminates its effect in labilizing the hydroxyl group for hydrogenation. This is shown by the fact that β-phenylpropionic ester (or cinnamic ester) was hydrogenated in a high yield to 3-phenylpropanol-1.

**Carbethoxy and Carbinol Groups.**—The effects of the carbethoxy and carbinol groups upon the hydrogenation of esters are considered together, because in this work it is impractical to distinguish the labilizing effect of

[4] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

the former from that of the carbinol group which is produced from it by hydrogenation.

One of the carbethoxy groups (or the resulting carbinol group) labilizes the hydrogenation of the carbinol group from the second carbethoxy group of malonic ester so that it is completely hydrogenated, there being no glycol produced but only ethyl propionate and its hydrogenation product, propyl alcohol. Similarly the monoethyl derivative of malonic ester is converted in a 78% yield to 2-methylbutanol-1. When this hydrogenation was interrupted before completion there was no evidence in the products that there was any glycol or hydroxy ester present. In a similar way neither β-hydroxybutyric ester nor its acetyl derivative hydrogenated to give a glycol. Moreover, the labilizing action of one oxygen-containing substituent not only manifests itself in labilizing the hydrogenation of the other, but in addition a carbon to carbon linkage is labilized so that the molecule is cleaved between the 2 and 3 carbon atoms as shown in the case of 2,2-dimethylacetoacetic ester.

If the carbethoxy groups are separated by two carbon atoms as in succinic ester, the effect of one upon the hydrogenation of the other is greatly minimized and tetramethylene glycol was produced in over 80% yield. In a similar way the oxygen containing groups in valerolactone exerted relatively little effect on each other so that pentanediol-1,4 was obtained in 78.5% yield, with only 8.1% *n*-pentanol. When the carbethoxy groups were still further apart as in glutaric and sebacic esters, the groups exerted no appreciable effect upon the hydrogenation of each other.

The hydrogenation of the methyl ester of α-phenylsuccinic acid to the glycol was not successful as a yield of only 12.6% was obtained, the main product (67.3%) being 3-phenylbutanol-1. It appears that the combined labilizing influence of the carbmethoxy and phenyl groups was too great to permit the preparation of the glycol in a satisfactory yield.

The experimental results referred to above are harmonious, indicating that phenyl, carbethoxy and carbinol groups labilize the hydrogenation of carbethoxy, carbonyl and carbinol groups when they are relatively near to these latter groups in the chain. However, in the case of ethyl lactate this generalization is invalid, for this ester yielded on reduction propanediol-1,2 in more than 90% yield.

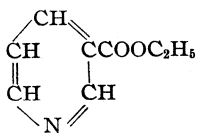
**Carbethoxy and Carbinol Groups and the Stability of Carbon to Nitrogen Linkages.**—The carbon to nitrogen linkages as in N-butylpiperidine are apparently quite stable under the experimental conditions used for the catalytic hydrogenation of esters since the amine was recovered unchanged after several hours at 250° and 260 atmospheres of hydrogen in the presence of an active copper–chromium–barium oxide catalyst. However, the oxygen-containing groups labilize the carbon to nitrogen linkage so that in certain compounds it is rather readily cleaved. In the

hydrogenation of ethyl β-piperidinopropionate the yield of the corresponding alcohol, 3-piperidinopropanol-1, was negligible, the chief products being piperidine, ethyl propionate, and N-ethyl and propylpiperidines. These products were, no doubt, formed as the result of the reactions noted below

$$C_5H_{10}NCH_2CH_2CO_2C_2H_5 + H_2 \longrightarrow C_5H_{10}NH + CH_3CH_2CO_2C_2H_5 \quad (I)$$
$$CH_3CH_2CO_2C_2H_5 + H_2 \longrightarrow C_3H_7OH + C_2H_5OH \quad (II)$$
$$C_5H_{10}NH + C_3H_7OH \longrightarrow C_5H_{10}NC_3H_7 + H_2O \quad (III)$$
$$C_5H_{10}NH + C_2H_5OH \longrightarrow C_5H_{10}NC_2H_5 + H_2O \quad (IV)$$

The presence of piperidine and ethyl propionate can hardly be accounted for except on the basis of equation I. Equation II represents the usual hydrogenation of an ester. The validity of equations III and IV is upheld by the finding that under the experimental conditions used for the hydrogenation of the ester, an 88% yield of N-hexylpiperidine was obtained from the reaction of piperidine and *n*-hexanol. The use of nickel as a catalyst for this type of reaction has recently been described.[5]

When ethyl nicotinate (I) was subjected to hydrogenation over a nickel or a copper–barium–chromium oxide catalyst, a cleavage occurred similar to that indicated in reaction 1. A mixture of bases was obtained but the chief product over nickel was 3-methyl-2-piperidone (III).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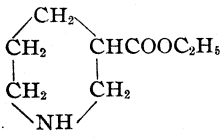
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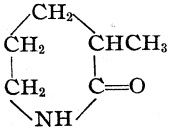

III

The carbethoxy group in nicotinic or nipecotic (II) ester is in the 3 position with respect to the nitrogen, just as it is in ethyl β-piperidinopropionate so that a similar cleavage of a nitrogen to carbon bond is not unexpected. Nicotinic ester would first be hydrogenated to nipecotic ester, this then must have undergone cleavage to the open-chain ester ($NH_2CH_2CH_2CH_2CH(CH_3)COOC_2H_5$), ethyl α-methyl-δ-aminovalerate. The interaction of the amino and carbethoxy groups of this ester would result in the formation of 3-methyl-2-piperidone.

As noted above, a carbethoxy group on a benzenoid ring was completely reduced to a methyl group, while ethyl hexahydrobenzoate was converted almost quantitatively to cyclohexylcarbinol. It therefore seemed possible that if the pyridinoid ring of nicotinic ester was saturated before attempting to reduce the carbethoxy group, it might be possible to prepare a 3-piperidinocarbinol from nicotinic ester. Nipecotic ester was therefore prepared by hydrogenating nicotinic ester over nickel at 165°. It was then alkylated with ethanol over a nickel catalyst according to the method

[5] Winans and Adkins, THIS JOURNAL, **54**, 306 (1932).

recently described.[5] The resulting ethyl N-ethylnipecotate ester was subjected to hydrogenation over a copper–barium chromium catalyst but the only product was N-ethyl-3-methylpiperidine, which was obtained in a 99% yield. This does not show, however, that it was formed as was *o*-cresol from methyl salicylate, that is, by the hydrogenation of the corresponding carbinol. It is more probable that it was formed through the cleavage of the ring and the formation of the piperidone as described above, followed by the hydrogenation of that cyclic amide. This hypothesis is borne out by the fact that an amide, N-caproylpiperidine was smoothly hydrogenated over the copper–barium–chromium oxide catalyst to N-*n*-hexylpiperidine in a 92% yield.

**Acids.**—The presence of free acid in the reaction mixture retards the hydrogenation as shown by the following experiment: five grams of copper–barium–chromium oxide catalyzed the reduction of 0.2 mole of *n*-butyl caproate to the extent of 75% in two minutes, and 100% in thirty-five minutes, whereas under exactly the same conditions 0.19 mole of *n*-butyl caproate and 0.01 mole of caproic acid was hydrogenated to the extent of 75% in thirty-eight minutes and 100% in 110 minutes. Furthermore, mixtures of caproic acid and *n*-butanol, or caproic acid and ethanol, could be hydrogenated only slightly, although the extent of esterification was 90–95%. However, the presence of a considerable amount of stearic acid in *n*-butyl stearate did not retard the hydrogenation to so great an extent.

**Alkyl Groups and Methanol.**—Methyl esters have been found to be unsatisfactory when a fast hydrogenation was desired. From Table I it is seen that methyl caproate hydrogenated 25% as rapidly as *n*-butyl caproate. Methanol cannot advantageously be used as a solvent, for dimethyl α-phenylsuccinate could not be hydrogenated in methanol, while in the pure state it was slowly hydrogenated. However, in the hydrogenation of butyl caproate, the presence of methanol merely retarded the rate (Table II). Possibly, methanol acts in the same inhibiting capacity as an acid. Brönsted has pointed out that methanol is 0.4 and ethanol only 0.06 as strong an acid as is water.[6] Although these figures are subject to numerical uncertainty, their great difference in magnitude suggests that methanol would be much more detrimental to the catalyst than ethanol.

The rates of hydrogenation of the nine caproic esters are perhaps best compared by considering the amount of hydrogen adsorbed after one and one-half hours (Table II). Although *sec.*-butyl caproate had a higher initial rate than *n*-butyl caproate, its final rate was less. Ethyl and lauryl caproates hydrogenated about 77% as rapidly as *n*-butyl caproate. Cyclohexyl caproate had by far the highest rate and it may also be seen from the data in Table I that the cyclohexyl ester of phenylacetic acid hydrogenated faster than did the ethyl ester. Since there was so little difference in the

[6] Brönsted, *Chem. Reviews*, **5**, 311 (1928).

rates of the *n*- and *sec.*-butyl esters, and such a large difference in the rates of the *n*-hexyl and cyclohexyl esters, the high rate of the cyclohexyl ester can hardly be attributed to the difference between primary and secondary alcohols, but rather to a specific effect of the cyclohexyl ring. Apparently, this effect is not entirely lost in the caproate of cyclohexylcarbinol, for this ester is next to cyclohexyl caproate in rate of hydrogenation.

**Pressure of Hydrogen.**—The effect of pressure of hydrogen on the rate of hydrogenation of ethyl laurate was shown by these experiments. Three grams of catalyst effected complete hydrogenation of 0.13 mole of ester at 250°, in seven hours at 106 ± 8 atm.; in one hour at 214 ± 9 atm.; and fifteen minutes at 333 ± 7 atm. Thus, from 100 atmospheres, a two-fold pressure increase caused a seven-fold increase in the rate, whereas a three-fold pressure increase caused a twenty-eight-fold increase in rate of hydrogenation.

**Temperature.**—The temperature required for hydrogenation of an ester over the copper–chromium oxide catalyst is within certain limits a function of the pressure of hydrogen, the activity of the catalyst, the ratio of the amount of ester to the amount of catalyst and of the nature and impurities present in the sample of ester under consideration. In general 250° has been found to be a suitable temperature for successfully carrying out the hydrogenation, although certain esters, such as cyclohexyl caproate, under the conditions chosen for test were rapidly and completely hydrogenated at 225°, while considerable hydrogen absorption occurred at 200° and lower. For example, ethyl laurate was hydrogenated for seven hours at 200° to determine the nature of the hydrogen absorption up to this temperature, and to see if aldehyde could be found in the product. The product contained 76.9% of the ethyl laurate used, and aldehyde tests with Tollens' and fuchsin reagents were negative. The amount of the hydrogen absorption indicated that 24% of the amount for complete reduction of the ester had been adsorbed. Therefore there is no evidence that even at 200° any stable intermediate reduction product is formed.

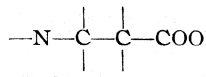
**Catalyst.**—The foregoing discussion has been based primarily upon the results obtained in the hydrogenation of esters over a copper–chromium oxide catalyst containing barium. The beneficial effect of barium in stabilizing the catalyst against reduction and consequent deactivation has been considered in the accompanying paper upon the preparation of catalysts. A comparison of the data in Table I on the hydrogenation of ethyl α-phenylbutyrate and ethyl phenylacetate indicates conclusively that magnesium and especially calcium are even more beneficial than is barium as a component of the catalyst. The rate of hydrogenation over these catalysts is much more rapid and in the case of ethyl phenylacetate the proportion of phenylethyl alcohol as compared with that of ethylbenzene is greatly increased.

## Summary

A number of esters with one or two carbalkoxy groups in the molecule have been hydrogenated to the corresponding alcohols or glycols in yields of 90–98%. The rate of hydrogenation is retarded by free acid or methanol and is considerably modified by the nature of the alkyl group in the carbalkoxy group. Thus cyclohexyl caproate was hydrogenated very much more rapidly than was ethyl caproate, while the latter was hydrogenated several times as rapidly as the methyl ester.

The presence of a phenyl, carbethoxy or carbinol group in the vicinity of a carbethoxy or carbinol group (except with ethyl lactate) labilized the cleavage of the carbon to oxygen linkage, the carbethoxy or carbinol group being thus hydrogenated to a methyl or methylene group. This reaction occurred almost exclusively when a phenyl group was adjacent to the carbethoxy group, or a carbethoxy or carbinol group was in the 2-position with respect to the ester group. When the phenyl group was in the 2-position there was a strong tendency for a similar reaction; however, by proper choice of experimental conditions and especially by the incorporation of magnesium or calcium into the catalyst, it was possible to avoid this reaction in large part.

A substituted amide, N-caproylpiperidine, was smoothly hydrogenated to the corresponding amine.

The nitrogen to carbon linkage in the group  is apparently readily cleaved under the conditions used for hydrogenation of the ester. With ethyl nipecotate the cleavage occurred over nickel as low as 165° and resulted in the formation of 3-methylpiperidine-2 or its hydrogenation products.

The rate of hydrogenation of ethyl laurate at 100, 200 and 300 atmospheres' pressure has been found to show a 28-fold increase over this range. The hydrogenation of esters under the conditions chosen for test proceeded smoothly at temperatures from about 200° upward.


MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

# BENZOIN REDUCTION. I. THE MECHANISM OF KETONE FORMATION. THE CASE OF BENZANISOIN

BY SANFORD S. JENKINS[1]

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It is generally known that symmetrical benzoins when treated with certain metals and acids under suitable conditions produce desoxybenzoins[2] and the reaction is usually explained by assuming a simple reduction of the alcoholic group —CHOH— of the keto-alcohol to the methylene group —$CH_2$—[3] according to the reaction $RCHOHCOR \xrightarrow[\text{[M Acid]}]{H_2} RCH_2COR$. Recently, however, the reduction of two unsymmetrical benzoins has been described[4a,b] and in each case *two isomeric* ketones were obtained. Since these benzoins are known to be definite compounds,[4b,5] the presence of isomeric desoxy derivatives cannot be accounted for on the usual assumption.[3]

Although benzanisoin has been studied already from many viewpoints by a number of investigators,[6] in the present work the reduction of this substance will be described and the results obtained along with those previously reported[4a,b] will be used as the basis of a new conception of the mechanism of benzoin reduction.

The starting material was obtained by condensing benzaldehyde and anisaldehyde by means of potassium cyanide. The compound melted at 106° and was shown to be authentic by comparison with a sample made by condensing mandelamide with *p*-methoxyphenylmagnesium bromide, according to the reaction

[1] Grafflin Scholar, 1930–1931.

[2] Zinin, *Ann.*, **119**, 180 (1861); Meyer and Oelkers, *Ber.*, **21**, 1295 (1888); Juillard and Tissat, *Arch. sci. phys. nat. Genevé*, [3] **25**, 387; *Chem. Centr.*, II, 166 (1891); Wachter, *Ber.*, **25**, 1727 (1892); Bader, *Chem. Z.*, **19**, 1939 (1895); Sudborough, *J. Chem. Soc.*, **71**, 218 (1897); Stobbe, *Ber.*, **35**, 911 (1902); Apitzsch and Metzger, *ibid.*, **37**, 1676 (1904); Apitzsch, *ibid.*, **40**, 1803 (1907); Irvine and Moodie, *J. Chem. Soc.*, **91**, 543 (1907); Buck and Jenkins, THIS JOURNAL, **51**, 2163 (1929).

[3] Gattermann, "Practical Methods of Organic Chemistry," The Macmillan Company, New York, 1928, p. 306.

[4] (a) Jenkins, Buck and Bigelow, THIS JOURNAL, **52**, 4495 (1930); (b) Jenkins, *ibid.*, **53**, 3115 (1931).

[5] Jenkins, Bigelow and Buck, *ibid.*, **52**, 5198 (1930).

[6] Meisenheimer and Jochelson, *Ann.*, **355**, 292 (1907); (b) Ekecrantz and Ahlquist, *Ark. Kem. Min. Geol.*, **3**, No. 13, 1–26 (1908); *J. Chem. Soc. Abs.*, **94**, 991 (1908); (c) Asahina and Terasaka, *J. Pharm. Soc. Japan*, **494**, 219 (1923); (d) McKenzie, Louis, Tiffeneau and Weill, *Bull. soc. chim.*, [4] **45**, 414 (1929); (e) Kinney, THIS JOURNAL, **51**, 1592 (1929); (f) Buck and Ide, *ibid.*, **53**, 3510 (1931); (g) Tiffeneau and Levy, *Bull. soc. chim.*, [4] **49**, 725 (1931).

$$C_6H_5CHOHCONH_2 \xrightarrow{3CH_3OC_6H_4MgBr} C_6H_5CH(OMgBr)C(OMgBr)NH(MgBr)C_6H_4OCH_3 \xrightarrow{3H_2O} C_6H_5CHOHCOC_6H_4OCH_3$$ [6d]

A number of derivatives was obtained. Thus when oxidized with Fehling's solution[4a,b] or copper sulfate in pyridine,[6e] the benzoin readily produced the benzil, which melted at 63°, and when reduced with sodium amalgam both hydro-[7a] and iso-hydrobenzanisoins[7a] were obtained. These glycols readily lost water when heated with a mixture of glacial acetic and concentrated hydrochloric acids and formed *p*-methoxybenzyl phenyl ketone, which has been described by Tiffeneau and Orékhoff.[7b] This ketone was reduced by means of sodium amalgam and produced *p*-methoxybenzylphenylcarbinol (not previously described) melting at 62°. This carbinol readily formed *p*-methoxystilbene[7a] when dehydrated with the acetic–hydrochloric acid mixture.

In a recent article[8] Buck and Ide have described the reduction of benzanisoin using tin and hydrochloric acid in alcoholic solution. They reported a yield of 87% of *p*-methoxybenzyl phenyl ketone and none of its isomer, benzyl *p*-methoxyphenyl ketone. The latter ketone certainly would be expected if the alcoholic group of the benzoin were attacked. Furthermore, it was stated that *p*-methoxybenzyl phenyl ketone formed both the *syn* and *anti* benzyl oximes when treated with hydroxylamine acetate in alcoholic solution.

In view of the unexpected results reported in the article just mentioned, a very careful reduction on a highly purified sample of benzanisoin was carried out, in the above manner, but *p*-methoxybenzyl phenyl ketone could not be obtained in a yield greater than 47%. The ketone was then treated with an excess of hydroxylamine acetate in alcoholic solution but, contrary to the statement of Buck and Ide, only the *anti* oxime was obtained and that in almost quantitative yield. There was not a trace of the *syn* oxime present.

Other crystalline material was isolated from the reduction mixture. By careful fractional crystallization one portion, melting sharply at 77°, was obtained, in small amount, but the greater portion of the solid melted between 60 and 65° and appeared to be a mixture of *p*-methoxybenzyl phenyl ketone and the fraction melting at 77°, since the melting point was raised when mixed with either of the latter substances.

The fraction melting at 77° was found to be pure benzyl *p*-methoxyphenyl ketone in the following manner. It was readily reduced with sodium amalgam to a substance melting at 58°. Benzyl-*p*-methoxyphenylcarbinol, which also melts at 58°, was prepared according to the method

[7] (a) Orékhoff and Tiffeneau, *Bull. soc. chim.*, [4] **37**, 1410 (1925); (b) Tiffeneau and Orékhoff, *ibid.*, [4] **37**, 430 (1925).

[8] Buck and Ide, THIS JOURNAL, **53**, 1536 (1931).

of Orékhoff and Tiffeneau[7a] by condensing anisaldehyde with benzylmagnesium chloride. The two compounds were found to be identical. The carbinol as prepared by either method readily lost water when heated with the acetic–hydrochloric acid solution and produced *p*-methoxystilbene.[7a] The reactions are

$$C_6H_5CH_2COC_6H_4OCH_3 \xrightarrow{H_2(Na,\ Hg)} C_6H_5CH_2CHOHC_6H_4OCH_3$$

$$C_6H_5CH_2MgCl \xrightarrow{CH_3OC_6H_4CHO} C_6H_5CH_2CH(OMgCl)C_6H_4OCH_3 \xrightarrow{H_2O} C_6H_5CH_2CHOHC_6H_4OCH_3$$

$$C_6H_5CH_2CHOHC_6H_4OCH_3 \xrightarrow{-H_2O(HAC,\ HCl)} C_6H_5CH{=}CHC_6H_4OCH_3$$

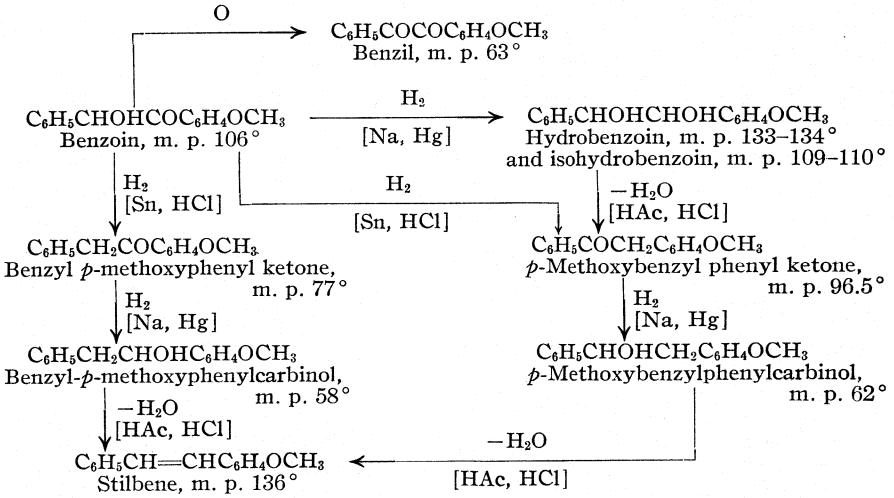
In order to prove the structure of the substance melting at 77° in a *direct* manner and beyond question, *p*-methoxybenzamide was condensed with benzylmagnesium chloride according to the general method of Béis[9] and after hydrolysis of the complex benzyl *p*-methoxyphenyl ketone was obtained. This compound also melted at 77° and when mixed with the substance above there was no depression of the melting point. The reactions are

$$CH_3OC_6H_4CONH_2 \xrightarrow{2C_6H_5CH_2MgCl} CH_3OC_6H_4C(OMgCl)NHMgClCH_2C_6H_5 \xrightarrow{2H_2O} CH_3OC_6H_4COCH_2C_6H_5$$

The ketone prepared in this manner was readily reduced with sodium amalgam and also produced the above carbinol. Thus it is seen that benzanisoin when reduced with tin and hydrochloric acid in alcohol solution yields both of the possible isomeric ketones as was to be expected.

The reactions which have been described above are represented in the following diagram.

DERIVATIVES OF BENZANISOIN

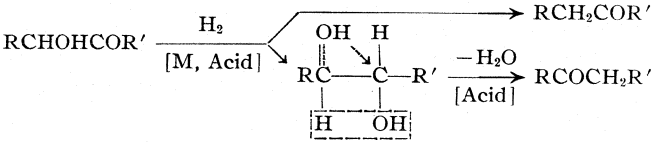



[9] Béis, *Compt. rend.*, **137**, 575 (1903).

Buck and Ide, in the paper mentioned above, prepared a substance which they thought was benzyl *p*-methoxyphenyl ketone by condensing phenylacetyl chloride and anisole in the presence of aluminum chloride. This reaction was first described by Ney[10] in 1888. He obtained a substance which melted at 76° and gave an oxime fusing at 111° but did not assign a position to the methoxyl group. The writer also carried out the reactions but obtained very small yields which varied in composition with different runs (see experimental part for details). In one run the material obtained was identical with the ketone prepared by the method of Béis, in another, however, the substances were unlike, as was shown by the melting points and the mixed melting point. This reaction thus affords another instance of the unreliability of the Friedel and Crafts method when applied to work of structure. This reaction is being studied further.

In view of the facts which have come to light in this and in the previous work which has been reported,[4a,b] it is certain that the usual conception of benzoin reduction with metals and acids is only partially true and that the reaction involves not only the alcoholic group of the keto-alcohol but the carbonyl group as well. Thus a certain amount of the glycol is produced which easily loses water in the acid medium to form the isomeric ketone.

The reactions may be represented as



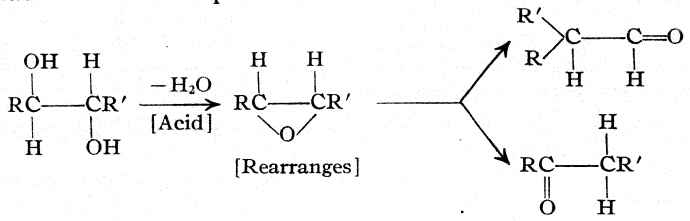

It is evident that glycols of this type might also lose water in such a way as to produce aldehydes or mixtures of these with the ketones and, indeed, this has been demonstrated in certain cases.[11] Orékhoff and Tiffeneau found that hydrobenzanisoin when dehydrated with sulfuric acid produced *p*-methoxydiphenylacetaldehyde[7a] along with *p*-methoxybenzyl phenyl ketone. One may also assume the presence of ethylene oxides as intermediate products in the formation of either ketones or aldehydes when these glycols are dehydrated. Thus, according to the rule of Breuer and Zincke,[12] "On abstraction of water, which can be effected by means of various reagents, all diatomic alcohols, containing OH groups attached to two neighboring carbon atoms, give first oxides (anhydrides or ethers) without any intramolecular changes, and then by further action of the reagent, ketones or aldehydes, or both."

[10] Ney, *Ber.*, **21**, 2450 (1888).

[11] Zincke, *ibid.*, **9**, 1769 (1876); Breuer and Zincke, *ibid.*, **11**, 72 (1878); Nevole *ibid.*, **9**, 448 (1876); Montagne, *Rec. trav. chim.*, **21**, 30 (1902); Tiffeneau and Orékhoff, *Bull. soc. chim.*, [4] **33**, 1832 (1923).

[12] Breuer and Zincke, *Ann.*, **198**, 141 (1879).

The reactions can be represented as




For the present purpose, however, these considerations are not pertinent. This work is being continued.

## Experimental

### Preparation of Benzanisoin

**First Method.**[6g]—To a solution of 40 g. of benzaldehyde, 52 g. of anisaldehyde and 115 cc. of 95% alcohol was added 12 g. of potassium cyanide dissolved in 80 cc. of water. The mixture was refluxed for one and one-half hours and allowed to stand in a cool place overnight. The crystalline material was filtered and washed twice with water and then with a small portion of cold alcohol. After three crystallizations from alcohol it weighed 29 g., which was 31% of the theoretical and melted at 106° (corr.).

**Second Method.**[6d]—In a 500-cc. round-bottomed flask were placed 3.0 g. of thin, bright, magnesium turnings, 22.4 g. of *p*-bromoanisole and 50 cc. of anhydrous ether. The reaction was started with a small crystal of iodine and after adding 50 cc. more of ether was allowed to proceed spontaneously for an hour. The flask was then heated for another hour over a 25-watt light. Mechanical stirring was employed throughout. To the solution 3.0 g. of finely powdered mandelamide in small portions was then added over a period of twenty minutes and the heating and stirring continued for eight hours. At the expiration of this time the reaction mixture was poured into 200 g. of a slush of ice and water containing 20 g. of concentrated sulfuric acid and thoroughly stirred. The ether layer was separated and the water layer extracted again with 100 cc. of ether. The combined extracts were washed with 100 cc. of 1% sodium carbonate solution and then with water. The ether was evaporated and the remaining yellow oil steam distilled. The residue was then dissolved in a small amount of alcohol and filtered hot. After standing in a cool place overnight the solution deposited 1.50 g. of snow-white needles melting at 102–104°. After two further crystallizations from alcohol the product melted at 106° (corr.). When this was mixed with the substance obtained by the *first method* there was no depression of the melting point.

***p*-Methoxybenzil.**[6e]—This diketone was readily prepared by oxidizing the keto-alcohol either with concentrated Fehling's solution[4a,b] or copper sulfate–pyridine solution, according to the method of Kinney.[6e] The first method, in which Fehling's solution was used, was found to be satisfactory. The benzoin dissolved in alcohol was heated on the water-bath with a small excess of reagent for thirty minutes, after which the solution was diluted with an equal volume of water and extracted twice with small portions of ether. After distilling the ether and crystallizing twice from 80% alcohol, the substance was obtained in a yield of 75–85% as yellow needles and melted at 63° (corr.).

**Hydro- and Isohydrobenzanisoin.**[7a]—These glycols were prepared by reducing the benzoin with sodium amalgam. Satisfactory yields were obtained by means of the following method. In a 125-cc. Erlenmeyer flask, in the lower edge of which a small bulb had been blown, was placed 0.01 mole (2.42 g.) of the benzoin and 40 cc. of 95%

alcohol. Solution was effected by warming and 15 g. (30% excess) of 4% sodium amalgam was then added. The mixture was mechanically shaken in an atmosphere of coal gas for five hours. By trapping the mercury in the bulb of the flask the solution was easily decanted and washed out with small portions of solvent. The alcohol was evaporated under reduced pressure and the substance dried. After recrystallizing twice from benzene the *hydrobenzoin* was obtained in a yield of 61% (1.50 g.), melting at 133–134°, as snow-white leaflets.

The mother liquors were evaporated to half-volume and allowed to stand in a cool place for several hours. About 0.2 g. of substance melting at 96–99° was obtained. The filtrate was then diluted with an equal volume of ligroin (Skelly solve "C") and placed in a cool place overnight. The solution deposited 0.40 g. of fine colorless needles which, after two further crystallizations from the benzene–ligroin solution, melted at 109–110° and was evidently impure *isohydrobenzanisoin*,[7a] as will be shown below.

### *p*-Methoxybenzyl Phenyl Ketone[7a,b]

**First Method.**—This ketone was produced in about 50% yield when either hydro- or isohydrobenzanisoin, as prepared above, was heated for twenty to thirty minutes with a mixture of 80% glacial acetic and 20% concentrated hydrochloric acids in the proportion of one part of glycol to 20–30 parts of the acid mixture. To obtain the ketone the solution was diluted with three volumes of water, neutralized with sodium carbonate, cooled and the solid filtered. After two crystallizations from alcohol it melted at 96.5° (corr.). On extracting the water mother liquors with ether and evaporating the latter, a colorless oil remained which was probably the *p*-methoxydiphenylacetaldehyde of Orekhoff and Tiffeneau[7a] but was not further investigated in the present work.

**Second Method.**—A mixture of 25 g. of benzanisoin (m. p. 106° corr.), 20 g. of mossy tin, 0.50 g. of hydrated copper sulfate, 100 cc. of alcohol and 70 cc. of concentrated hydrochloric acid was refluxed for six hours and filtered hot. After standing for some time in a cool place the crystalline material was filtered, washed twice with small portions of alcohol and dried *in vacuo* It weighed 14.5 g. and melted at 86–92°. After two further crystallizations from alcohol, the substance was obtained as colorless plates which weighed 9.30 g. and melted at 96.5° (corr.). The filtrates from which the crystals were obtained were combined, diluted with an equal volume of water and most of the alcohol distilled. The solution was then made slightly alkaline with sodium carbonate, cooled and filtered. The precipitate was washed with water, sucked dry and extracted three times with 50-cc. portions of boiling alcohol. The solution was then evaporated to a volume of about 100 cc. and filtered hot. On standing the solution deposited 1.80 g. more of the ketone which after a further crystallization melted at 95–96°. The total yield of substance amounted to about 47%.

### Benzyl *p*-Methoxyphenyl Ketone

**First Method.**—The filtrate above was evaporated to a volume of about 50 cc. On cooling 9.10 g. of material, melting at 55–60°, was obtained. After evaporating to a volume of about 20 cc., the filtrate deposited a further 0.50 g. of material which melted at 52–61°. The mother liquors were then evaporated *in vacuo* and an oily residue remained which smelled strongly of benzaldehyde but was not further studied. The two crops of crystals were combined and recrystallized from ligroin–benzene (5:1) solution. On standing the solution deposited two types of crystals; one portion consisted of flakes, the other was made up of clusters of thick prisms radiating from a common center. The latter were mechanically separated and recrystallized from a small portion of the ligroin–benzene mixture and 0.50 g. of material melting at 76–77°

was obtained which after another crystallization melted at 77°. The other portion (flakes) melted at 61–65°. When this was mixed with either *p*-methoxybenzyl phenyl ketone or the substance melting at 77° the melting point was raised. As will be shown below, the substance melting at 77° proved to be benzyl *p*-methoxyphenyl ketone; that which melted at 61–65° was a mixture of the two ketones which was not further studied.

**Second Method.**—In order to prove the structure of the substance melting at 77°, obtained above, the general method of Béis[9] was employed. In a 500-cc. three-necked round-bottomed flask was placed 7.5 g. of magnesium turnings and a small crystal of iodine. The flask was fitted with a dropping funnel containing 38 g. of benzyl chloride dissolved in 100 cc. of anhydrous ether. A few cc. of this solution was added to the magnesium and after the reaction had started 50 cc. more of ether was added. The benzyl chloride–ether solution was then slowly added during the course of thirty minutes, after which the solution was heated over a twenty-five watt light for an additional hour. To the mixture 10 g. of finely powdered *p*-methoxybenzamide was added in small portions during twenty minutes and the whole refluxed for eight hours. The mixture was then poured into 200 g. of a slush of ice and water containing 20 g. of concentrated sulfuric acid. After thorough stirring the ether was separated and the water again extracted with 100 cc. of ether. The combined extracts were steam distilled and the residue dissolved in ether and dried over anhydrous sodium sulfate. After distilling the ether the residue was dissolved in ligroin and filtered hot. On standing 3.0 g. of material melting at 69–74° was obtained. After two further crystallizations from ligroin it melted at 77° (corr.). When this was mixed with the substance obtained in the *first method*, there was no depression of the melting point.

*Anal.* Calcd. for $C_{15}H_{14}O_2$: C, 79.60; H, 6.24. Found: C, 79.40; H, 6.41.

***p*-Methoxybenzylphenylcarbinol.**—To a solution of 2.26 g. (0.01 mole) of the ketone in 40 cc. of warm alcohol was added 15 g. of 4% sodium amalgam (about 30% excess). The mixture was shaken in an atmosphere of coal gas (apparatus and technique described above) for five hours. The mercury was separated, the alcohol evaporated under reduced pressure and 100 cc. of water added. The product was extracted with ether and the solution dried over anhydrous sodium sulfate. After evaporating the ether the carbinol was recrystallized from ligroin. It weighed 1.85 g., which was 81% of the theoretical, and melted at 56–59°. The substance was moderately soluble in hot water, from which it separated on cooling as long needles, and was quite soluble in ether and alcohol. From ligroin it crystallized as thick colorless prisms and when pure melted at 62° (corr.).

*Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.90; H, 7.06. Found: C, 78.76; H, 6.98.

### Benzyl-*p*-methoxyphenylcarbinol[7a]

**First Method.**—This carbinol was obtained by reducing *p*-methoxybenzyl phenyl ketone with sodium amalgam according to the method already described. The substance was obtained in a yield of 80–85% and when purified by crystallization from ligroin it melted at 58° (corr.).

**Second Method.**—Anisaldehyde was condensed with benzylmagnesium chloride according to the directions of Orékhoff and Tiffeneau.[7a] The substance thus obtained, after several crystallizations from ligroin, melted at 58° (corr.) and when mixed with that obtained by the *first method* there was no depression of the melting point.

***p*-Methoxystilbene.**—This compound was obtained in 80–85% yield by heating for twenty to twenty-five minutes either *p*-methoxybenzylphenylcarbinol or benzyl-*p*-methoxyphenylcarbinol with 20 parts of the acetic–hydrochloric acid mixture mentioned above. Recrystallized from alcohol it melted at 135° (corr.).

**p-Methoxybenzyl Phenyl Ketone Oxime.**[7a,8]—In a small Erlenmeyer flask (125-cc.) was placed 2.00 g. of *p*-methoxybenzylphenyl ketone, 2.00 g. of hydroxylamine hydrochloride, 3.00 g. of potassium acetate and 50 cc. of alcohol. The flask was corked and left overnight. The following morning the mixture was heated on the water-bath for three hours and then diluted with 100 cc. of water. After cooling, filtering and washing with water, a mass of colorless needles was obtained which on drying *in vacuo* weighed 2.075 g. and melted at 132–133.5° (corr.). To the mother liquors 100 cc. more of water was added and another crop of crystals was obtained which weighed 0.049 g. and melted at 129–132° (corr.). When the two substances were mixed there was no depression of the melting point. The combined yield obtained was over 99%. Recrystallized from ligroin the compound melted sharply at 134° (corr.).

**p-Methoxyphenylacetanilide.**[8]—To 0.50 g. of the above oxime was added 30 cc. of anhydrous ether and 1.2 g. of phosphorus pentachloride. The mixture was shaken for twenty minutes and poured into 50 cc. of water. After evaporating the ether and cooling, the crude anilide was filtered and recrystallized from a small amount of 75% alcohol. It weighed 0.30 g. and melted at 115.8° (corr.).

The anilide was hydrolyzed by heating for thirty minutes with 20 cc. of concentrated hydrochloric acid. The solution was made alkaline with sodium carbonate and extracted with ether. From the ether solution aniline was obtained and was identified by its odor and conversion into acetanilide. The water solution was acidified and the *p*-methoxyphenylacetic acid separated and identified by its melting point and crystalline structure.[13]

**Benzyl p-Methoxyphenyl Ketone Oxime.**—This oxime was prepared from the corresponding ketone in a manner similar to that above and was obtained in a yield of 95%. When crystallized from ligroin it melted at 114° (corr.).

*Anal.* Calcd. for $C_{15}H_{15}NO_2$: N, 5.80. Found: N, 5.67.

**Friedel and Crafts Reaction.**[10] **Examples.**—To a solution of 20 g. of phenylacetyl chloride, 16 g. of anisole and 80 g. of carbon disulfide, 20 g. of aluminum chloride (anhydrous, Baker's C. P.) was added in small portions during the course of thirty minutes. The solution was then heated on the water-bath for three hours and after treatment with ice water was steam distilled. The yellow oil remaining was washed with 5% sodium hydroxide solution and then with water. Two methods were employed for purifying the substance.

(1) The oil was dissolved in alcohol and allowed to stand in a cool place overnight. From the solution four grams of material was obtained which after two further crystallizations from alcohol melted at 73–74° (corr.).

(2) The oil was fractionated *in vacuo*. The greater portion failed to distil at 200° under a pressure of 3–5 mm. A fraction of about two grams which distilled between 120–140° at 3–5 mm. was obtained and when twice crystallized from alcohol melted at 75–76° (corr.). This substance was different from that obtained by *Method 1* as was shown by a mixed melting point determination, but was identical with benzyl *p*-methoxyphenyl ketone obtained in the Grignard reaction mentioned above.

The writer wishes to thank Professor E. Emmet Reid for his interest and help in this work.

## Summary

1. A new conception of the mechanism of benzoin reduction is advanced.

[13] Cain, Simonsen and Smith, *J. Chem. Soc.*, **103**, 1035 (1913).

2. It has been shown that benzanisoin when reduced under suitable conditions produces not only *p*-methoxybenzyl phenyl ketone but also its isomer, benzyl *p*-methoxyphenyl ketone. Only the *anti* benzyl oxime was obtained from *p*-methoxybenzyl phenyl ketone.

3. By means of the Grignard reaction the structure of benzyl *p*-methoxyphenyl ketone has been determined by two independent methods.

4. A number of derivatives of benzanisoin has been obtained. A new carbinol was prepared and characterized.

5. The reliability of the method of Friedel and Crafts in structural work of this nature is brought into question.

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, THE GOODYEAR TIRE & RUBBER CO.]

# THE REACTION OF DIAZONIUM SALTS ON SODIUM ALKYL DITHIOCARBAMATES

BY A. M. CLIFFORD AND J. G. LICHTY

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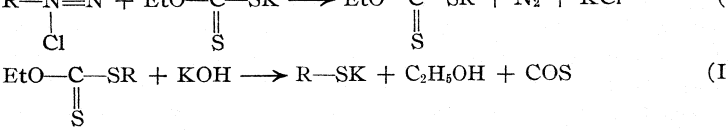
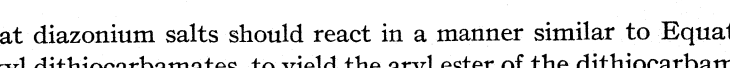
Bernthsen and Friese[1] and also Billeter and Strohl[2] were apparently among the first to describe esters of disubstituted dithiocarbamic acids and reported the synthesis and properties of the ethyl and the phenyl esters of ethylphenyldithiocarbamic acid. Since these publications, little has appeared in the literature concerning this class of compounds. Certain nitro substituted aryl esters of dialkyl dithiocarbamic acids are claimed in patents issued to Cadwell,[3] and obtained by reaction between dithiocarbamate and an aryl compound containing reactive halogen.

A reaction has been found in this Laboratory which is capable of yielding the unsubstituted, as well as the substituted, aryl esters of alkyl dithiocarbamic acids.

Leuckart's excellent reaction[4] for the preparation of thiophenols sug-



(I)



(II)

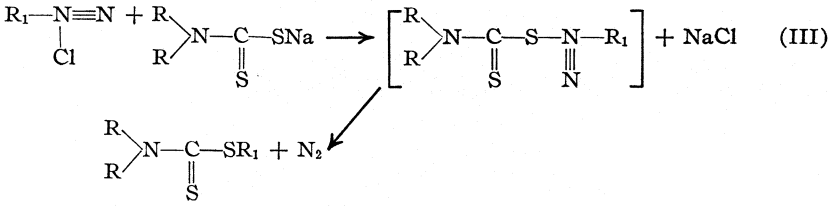
gested that diazonium salts should react in a manner similar to Equation I with alkyl dithiocarbamates, to yield the aryl ester of the dithiocarbamate

[1] Bernthsen and Friese, *Ber.*, **15**, 568 (1882).

[2] Billeter and Strohl, *ibid.*, **21**, 102 (1888).

[3] Cadwell, U. S. Patents, 1,726,646, 1,726,647, 1,726,648, Sept. 3, 1929; 1,736,429, Nov. 19, 1929.

[4] Leuckart, *J. pract. Chem.*, [2] **41**, 179 (1890).



That such a reaction does take place has been proved, and, furthermore, it provides a convenient method for obtaining such esters. It is the purpose of this paper to relate our experiences on the esterification of the dithiocarbamates derived from dimethylamine, diethylamine and piperidine by the above described reaction.

In Equation III postulated above an intermediate product is indicated as playing a part in the reaction. Good evidence for the formation of an intermediate, in most cases very unstable, product was the isolation of an explosive material from the reaction between sodium dimethyldithiocarbamate and *p*-nitrophenyldiazonium chloride. This material lost its detonating tendency after exposure in the open air for several hours, and on boiling in alcohol yielded *p*-nitrophenyldimethyldithiocarbamate. Königs[5] likewise has indicated that diazonium salts of certain acids may be isolated, for example, benzenediazonium benzene sulfinate, $C_6H_5N_2SO_2$-$C_6H_5$, which appears as a fairly stable compound.

## Experimental

**Preparation of Diazonium Salts.**—One mole of the amine and two moles of hydrochloric acid, using approximately 10% acid of known concentration, were diluted to 1500 cc. The solution was maintained at 0–5° and stirred during the addition of a solution of 2% excess of sodium nitrite in 300 cc. of water. At the end of the addition of the sodium nitrite a solid was formed. While this was not desirable it was unavoidable inasmuch as an excess of acid would decompose the dithiocarbamate during the coupling process.

**Preparation of Sodium Dithiocarbamates.**—A 20% aqueous solution containing one mole of the amine maintained at 10° or below was stirred during the slow addition of 1.05 moles of carbon disulfide. This was followed by the slow addition of one mole of sodium hydroxide of approximately 10% concentration. The product was then allowed to warm to room temperature. In the preparation of piperidiniumpentamethylenedithiocarbamate, water was added until the salt was completely dissolved. The aqueous solution was decanted from the excess carbon disulfide. This carbon disulfide was washed with water several times by decantation, adding the washings to the aqueous solution.

**Coupling.**—The cold aqueous solution of the diazonium salt was added in equimolecular proportion, dropwise, to the well-stirred aqueous dithiocarbamate solution at room temperature. Each drop of the diazonium solution added caused an immediate, violent evolution of nitrogen with only a small liberation of heat. The behavior on addition of *p*-nitrophenyldiazonium chloride, however, was an exception, as only a very small quantity of nitrogen was evolved, and a solid product separated which, when

[5] Königs, *Ber.*, **10**, 1533 (1877).

dry, was explosive. In most instances the evolution of nitrogen was accompanied by the separation of a reddish-yellow oily layer. It was customary to allow the reaction mixture to stand for twelve to sixteen hours, during which time partial crystallization of the product usually occurred.

The crystalline portion of the reaction product was filtered off and washed with a small quantity of diethyl ether to remove adhering oil. The solid material thus obtained was a relatively pure ester. The liquid portion of the product was taken up with ether and to this solution was added the ether extracts of the aqueous layer. The ether solution was dried with calcium chloride, filtered and the solution evaporated by gentle warming, then set aside to crystallize. The crystals thus obtained were filtered off, washed as before, combined with the first crop, and the whole recrystallized from alcohol. Large white or pale yellow well-defined crystals were obtained. The *p*-tolyl esters in particular formed perfect, massive prisms of one centimeter or more across. The oily filtrate was subjected to distillation under reduced pressure; this process apparently caused partial decomposition as only after distillation was the odor of thiophenols noticeable. The fractions obtained usually solidified, completely or in part. Further purification of the various fractions by repeated crystallizations yielded the substituted ammonium dithiocarbamate, the disulfides and thioureas, in addition to more of the ester.

When a solid product was obtained by the interaction of the diazonium salt on the dithiocarbamate, it was removed by filtration, dried and separated into its various constituents by a series of fractional crystallizations.

Data pertaining to the compounds obtained by the above procedure are given in the table.

TABLE I

PRODUCTS OF REACTION OF DIAZONIUM SALTS

| No. | Diazonium salt derived from | Amine used Moles, g. | | Yield of crude product, g. | (DTCB = dithiocarbamate) Miscellaneous compounds | M. p., °C. |
|---|---|---|---|---|---|---|
| | | | | | DERIVATIVES OF SODIUM DIMETHYLDITHIOCARBAMATE | |
| 1 | Aniline | 1.2 | 111.6 | 209 | Dimethylammonium dimethyl-DTCB | 127–129[a] |
| | | | | | Tetramethylthiourea | 78–79[b] |
| | | | | | Diphenyl disulfide (17 g.) | 60–61[a] |
| 2 | *p*-Toluidine | 1.2 | 128.4 | 227.8 | | |
| 3 | *o*-Toluidine | 1.2 | 128.4 | 193.2 | Dimethylammonium dimethyl-DTCB | 127–129[a] |
| | | | | | Tetramethylthiourea | 78–79 |
| 4 | *p*-Bromoaniline | 0.8 | 137.6 | 184.5 | 4,4′-Dibromodiphenyl disulfide | 93–94[c] |
| 5 | *p*-Nitroaniline | 0.8 | 110.4 | 130.5 | | |
| | | | | | DERIVATIVES OF SODIUM DIETHYLDITHIOCARBAMATE | |
| 6 | Aniline | | 93 | 193.2 | Diethylammonium diethyl-DTCB | 81–82[a] |
| 7 | *p*-Toluidine | | 107 | 209.7 | Diethylammonium diethyl-DTCB | 81–82[a] |
| | | | | | DERIVATIVES OF SODIUM PENTAMETHYLENEDITHIOCARBAMATE | |
| 8 | Aniline | | 93 | 213.6 | Diphenyl disulfide (0.4 g.) | 60–61[a] |
| | | | | | Piperidiniumpentamethylene-DTCB (8.8 g.) | 169–170[a] |
| 9 | *p*-Toluidine | | 107 | 226.5 | Piperidiniumpentamethylene-DTCB (30.6 g.) | 169–170[a] |

[a] These compounds when mixed with a pure sample synthesized by other methods gave no depression of the melting points.

[b] *Anal.* Calcd. for $C_5H_{12}N_2S$: N, 21.21. Found: N, 20.86, 20.93. Delépine [*Bull. soc. chim.*, **7**, 988–993 (1910)] reports a melting point of 78° for tetramethythiourea.

[c] *Anal.* Calcd. for $C_{12}H_8Br_2S_2$: Br, 42.54. Found: Br, 42.00, 41.90. Hübner and Alsberg [*Ann.*, **156**, 328 (1870)] reports a melting point of 93.5° for 4,4′-dibromodiphenyl disulfide.

TABLE I (*Concluded*)

| No. | Ester (dithiocarbamate) | Yield, g. | M.p., °C. | Formula | Analyses: Nitrogen, % Calcd. | Nitrogen, % Found | | Sulfur, % Calcd. | Sulfur, % Found | |
|---|---|---|---|---|---|---|---|---|---|---|
| | DERIVATIVES OF SODIUM DIMETHYLDITHIOCARBAMATE | | | | | | | | | |
| 1 | Phenyldimethyl- | 75.5 | 94–95 | $C_9H_{11}NS_2$ | 7.11 | 7.05 | 7.05 | 32.48 | 32.45 | 32.30 |
| 2 | *p*-Tolyldimethyl- | 64.5 | 112–113 | $C_{10}H_{13}NS_2$ | 6.63 | 6.55 | 6.41 | 30.33 | 30.40 | 30.55 |
| 3 | *o*-Tolyldimethyl- | 46.5 | 81–82 | $C_{10}H_{13}NS_2$ | 6.63 | 6.65 | 6.57 | 30.33 | 30.00 | 29.90 |
| 4 | *p*-Bromophenyldimethyl- | 20 | 120–121 | $C_9H_{10}NS_2Br_2$ | 5.09 | 5.10 | 5.10 | 23.19 | 23.15 | 23.30 |
| 5 | *p*-Nitrophenyldimethyl- | 50.3 | 154 | $C_9H_{10}O_2N_2S_2$ | 11.57 | 11.34 | 11.34 | 26.44 | 25.85 | 25.95 |
| | DERIVATIVES OF SODIUM DIETHYLDITHIOCARBAMATE | | | | | | | | | |
| 6 | Phenyldiethyl- | 38.6 | 46 | $C_{11}H_{15}NS_2$ | 6.22 | 6.15 | 6.08 | 28.44 | 28.30 | 28.40 |
| 7 | *p*-Tolyldiethyl- | 73.9 | 77–78 | $C_{12}H_{17}NS_2$ | 5.86 | 5.88 | 5.81 | 26.77 | 27.00 | 26.90 |
| | DERIVATIVES OF SODIUM PENTAMETHYLENEDITHIOCARBAMATE | | | | | | | | | |
| 8 | Phenylpentamethylene- | 78 | 116–117 | $C_{12}H_{15}NS_2$ | 5.90 | 5.95 | 5.88 | 27.00 | 27.30 | 27.30 |
| 9 | *p*-Tolylpentamethylene- | 90.4 | 118–119 | $C_{13}H_{17}NS_2$ | 5.57 | 5.46 | 5.32 | 25.50 | 25.85 | 25.95 |

Preliminary evidence indicates that nitrogen is retained in the reaction products of diazonium salts with the alkali metal salts of aliphatic and aromatic carboxylic acids.

**Acknowledgment.**—The authors desire to express their thanks to Messrs. R. P. Dinsmore and L. B. Sebrell for permission to publish this work.

## Summary

1. Diazonium salts react with sodium alkyl dithiocarbamates, giving as the main product aryl esters of the dithiocarbamic acids.

2. A series of new aryl esters of dimethyl-, diethyl- and pentamethylenedithiocarbamic acids has been described.

3. Other compounds isolated from the reaction products include the aryl disulfides, the substituted ammonium alkyl dithiocarbamates and in some cases an alkyl substituted thiourea.

AKRON, OHIO

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

# A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. VI. INTERMEDIATE STAGES[1]

BY W. H. HUNTER AND R. B. WHITNEY

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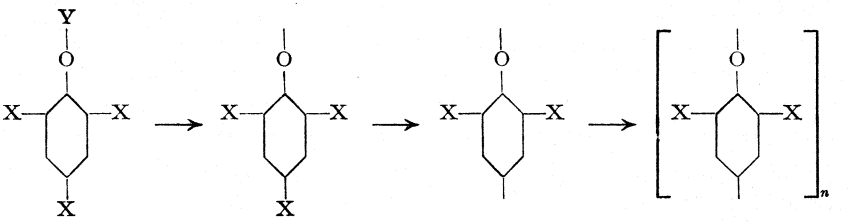
In the earlier papers of this series it was shown that silver salts of trihalogenated phenols in the presence of ethyl iodide, hot benzene, or other catalysts, and also the alkali salts with small amounts of bromine or iodine, decompose to form a metal halide and an amorphous substance of high molecular weight. The latter has the formula $(OC_6H_2X_2)_n$, and the name polydihalogenophenylene oxide has been given it.[2]

Tribromophenol bromide, shown by Lauer to be the hypobromite of tribromophenol,[3] loses bromine slowly on standing and gives the same polymer. Mercury accelerates this reaction.[4] Similar amorphous oxides are formed by the oxidation of trihalogenated phenols.[5]

To account for these facts the hypothesis of the univalent (Type A) radicals and the bivalent (Type B) radicals was developed, according to which the general scheme is




This hypothesis has also proven useful in the study of the various products of oxidation of halogenated phenols.

Thus the formation of dinuclear quinones is accounted for by the union of two Type B radicals in the quinoid form, as for example in the interesting oxidation of tribromoresorcinol by Davis and Hill.[6]

Furthermore the production of such compounds as di-(trichlorophenoxy)-

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by R. B. Whitney in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1927. The manuscript for this paper was read by Dr. W. H. Hunter shortly before his death on August 19, 1931. Some final revisions suggested by him were not made until after his death.—R. B. W.

[2] Hunter and Woollett, THIS JOURNAL, **38**, 1761 (1916); Hunter and Seyfried, *ibid.*, **43**, 151 (1921).

[3] Lauer, *ibid.*, **48**, 442 (1926).

[4] Hunter and Woollett, *ibid.*, **43**, 131 (1921).

[5] Hunter and others, unpublished work, and THIS JOURNAL, **48**, 1618 (1926).

[6] Davis and Hill, *ibid.*, **51**, 493 (1929).

quinone by the oxidation of trichlorophenol[7] seems to require the existence of both Type A and Type B radicals.

In the present work, further evidence for the existence of these radicals has been obtained from a study of the electrolysis of the silver salts of trihalogenated phenols in pyridine. The usual characteristic blue color, observed generally during the various decompositions, developed rapidly at the anode, and the amorphous polyphenylene oxide was isolated.

The work to be described in the remainder of this paper was undertaken in order to elucidate more clearly the nature of these intermediate stages.

It was known that both hydroquinone and triphenylmethyl discharge the intermediate blue color. In quantitative experiments, however, we could not find conditions under which more than one one-hundredth of an equivalent of either reagent was required to decolorize the solution, although the blue color, after being just discharged, would reappear, and this could be repeated several times.

Further experiments showed that the blue solution is instantaneously decolorized by unhalogenated or monohalogenated phenols and aromatic amines, an interesting exception being phloroglucinol. Alcohols and acids, however, do not have this effect.

**Plan of Attack.**—In the hope of arresting the decomposition at one of its intermediate stages, reagents capable of destroying the blue color were introduced before the reaction was started. The experimental conditions were varied, but in all cases were such that the amorphous oxide would have been formed if the inhibiting reagent had been absent.

The silver salts could not be studied in this way as they were found to be reduced by triphenylmethyl and by phenol. In the latter case there was formed an amorphous product similar to the usual amorphous oxide but containing less halogen. The percentage of halogen in it increased roughly with decreasing amount of added phenol. It seems likely that the reaction

$$C_6H_2Br_3OAg + C_6H_5OH \longrightarrow C_6H_2Br_3OH + C_6H_5O- + Ag$$

occurring simultaneously with the usual decomposition would introduce unhalogenated phenyl groups into the polymer.

The alkali salts, on the other hand, do not decompose by themselves even after long heating at the temperature of boiling xylene. Their decomposition by iodine was studied by Hunter and Seyfried,[2] who showed that the usual amorphous oxide is formed in water, benzene, or acetone; that the rate of decomposition depends upon the amount of iodine used, although the iodine is recovered at the end; that the iodine attacks the sodium atom directly; and that loss of ortho or para halogen occurs later.

We chose to study this reaction in the presence of reagents which discharge the blue intermediate color.

**Discussion of Experimental Results.**—The result in each case was that

[7] Hunter and Morse, THIS JOURNAL, **48**, 1615 (1926).

no amorphous oxide was formed, and that an iodination occurred, either of the inhibiting reagent or the solvent.

**Iodination of Inhibiting Reagents.**—Sodium trichlorophenolate was dissolved in an excess of dry, colorless aniline, and two equivalents of iodine were added. After a few minutes' gentle warming, the iodine color faded, and a white precipitate of sodium iodide formed. From the aniline solution an 85% yield of *p*-iodoaniline was obtained. No trace of the polyphenylene oxide was found. Ninety-five per cent. of the original trichlorophenol was recovered.

In order to learn whether any loss of halogen from the trichlorophenol had occurred, the *p*-iodoaniline fraction was examined carefully for chlorine but none was found.

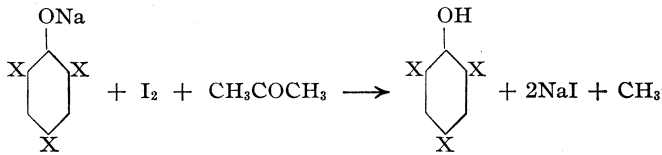
Sodium tribromophenolate gave similar results.

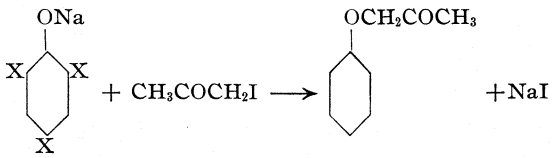
An equally smooth reaction was observed when iodine was added to solutions or suspensions of the sodium trihalogenophenolate under each of the following conditions: (1) in solution in molten phenol, (2) in suspension in dry ether containing one equivalent of phenol, (3) in suspension in dry ether containing one equivalent of dimethylaniline.

**Iodination of Solvent.**—Sodium or potassium trihalogenophenolates were dissolved in acetone (or acetophenone) in which one equivalent of phenol or dimethylaniline was present. Two equivalents of iodine were added. The iodine color faded, and with gentle warming disappeared in less than an hour.

The reaction products were sodium iodide, about half of the original trihalogenated phenol, and an acidic (in the case of dimethylaniline a basic) organic oil containing a small amount of iodine, and a white crystalline substance insoluble in both acids and bases. In each case this was found to be the acetonyl ether of the trihalogenated phenol. No amorphous oxide was found.

The yields of acetonyl ether varied between 40 and 70% of the amount required by the reactions



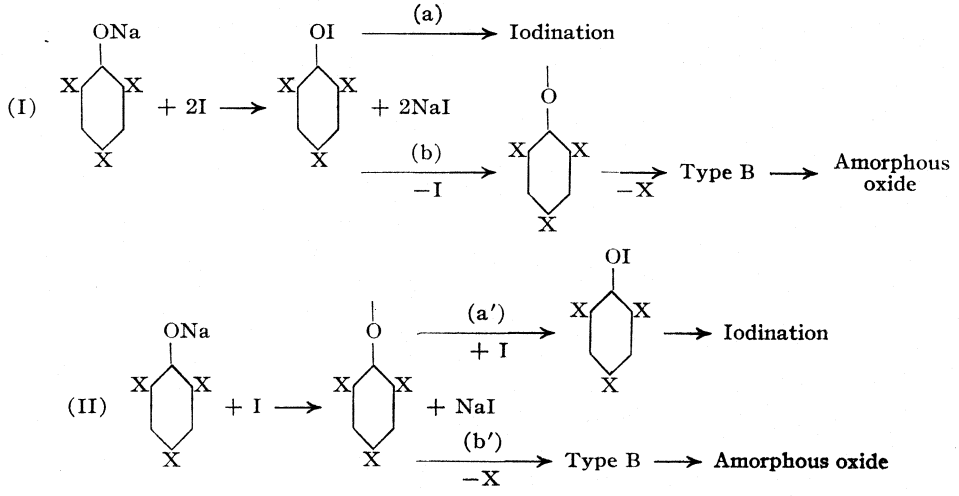

When mesitol was used in place of phenol, a 90% yield of the acetonyl ether was found, a considerable quantity (about half) of the mesitol was recovered, and there was no iodophenol residue.

It was found that no more than two equivalents of iodine would react. If the amount of the inhibiting reagent (phenol or dimethylaniline) was decreased, the formation of amorphous oxide was still prevented, until only one-fourth of an equivalent of the reagent was present, when a small amount of the polymer formed.

**Mechanism.**—For these reactions to be of significance in the study of the halogenated phenol salts, it must, of course, be shown that we are not dealing with a direct reaction of the iodine upon the phenol, amine, or acetone. For this reason, parallel reactions were run in representative cases, omitting the halogenated phenol salts. Under these circumstances practically no reaction occurred. The direct iodination of aniline apparently took place after a long time, but gave much tar and practically no pure product. Hofmann[8] had reported this reaction, but later investigators[9] have been unable to obtain more than a minute amount of iodoaniline in this way.

That we are not dealing with a case of shifting an equilibrium by the removal of hydrogen iodide by the alkali salt is shown in the case of the acetone reaction, where sodium trihalogenophenolate and iodine cannot alone halogenate the acetone. Moreover, the action of iodine upon the sodium salts is fairly rapid, so that the complete absence of any amorphous oxide is independent evidence that an appreciable part of the iodination goes by way of an interaction between the iodine and the sodium salt.

Since the absence of any halogen excepting iodine in the products makes it unlikely that the Type B radical participates in these reactions, there are essentially two possible mechanisms




[8] Hofmann, *Ann.*, **67**, 61 (1848).

[9] Mills, *ibid.*, **176**, 354 (1875); Chattaway and Constable, *J. Chem. Soc.*, **105**, **124** (1914).

It might seem that a distinction between these mechanisms would be meaningless. However, there is one definite piece of evidence for mechanism II, and against mechanism I, namely, that in the analogous case of catalysis of the decomposition by bromine, a small amount of bromine causes fairly rapid production of the amorphous oxide, whereas the hypobromite of tribromophenol (tribromophenol bromide) is moderately stable under the same conditions, and loses halogen only slowly.

The simplest explanation of the surprising action of phenol or dimethylaniline in acetone seems to be that they can stabilize, *i. e.*, prevent loss of halogen from the Type A radical, until it has had time to form the hypoiodite (reaction IIa). The hypoiodite then iodinates the acetone in preference to the inhibiting reagent merely because of the greater quantity of the former.

## Experimental Part

**Substances which Discharge the Intermediate Blue Color.**—A small crystal of iodine was added to a dilute acetone solution of the potassium salt of tribromoresorcinol monomethyl ether. Solutions of various substances in acetone were added to portions of the resulting blue-green solution.

Those which discharged the color were aniline, mono- and dimethylaniline, α-naphthylamine, *p*-iodoaniline, benzidine, phenol, hydroquinone, hydroquinone monomethyl ether, resorcinol, resorcinol monomethyl ether, and α-naphthol and picric acid. In all these cases three or four drops of a dilute solution was sufficient. Those which had no effect upon it were tribromoaniline, acetamide, urea, *sym.*-diphenylurea, phthalimide, benzamide, tri- and pentahalogenated phenols, phloroglucinol, phenylethylcarbinol, allyl alcohol, benzoic acid, *p*-nitrobenzoic acid, *p*-chloronitrobenzene, hydroquinone dimethyl ether, anisole.

**Reduction of Silver Salts by Triphenylmethyl.**—An attempt was made to carry out the thermal decomposition of the silver salt of tribromophenol in the presence of triphenylmethyl. Fifteen grams of the silver salt was suspended in 100 cc. of dry benzene in an inert atmosphere. An excess (about two equivalents) of triphenylmethyl was introduced, and the suspension was stirred and warmed by steam for six hours. The red color of the silver salt disappeared, and a black precipitate formed. The solution was decanted and the precipitate washed with benzene. Upon treatment with dilute nitric acid, the precipitate was mostly dissolved, and approximately 4.5 g. of silver chloride was obtained from the solution (one equivalent). The combined benzene solutions were stirred in the air and allowed to stand overnight. The triphenylmethyl peroxide was filtered off, and the benzene evaporated under reduced pressure. The residue was a sticky mass. Continued extraction in a Soxhlet apparatus with fractol left a residue of triphenylmethyl peroxide. Upon evaporation the fractol solution gave a dirty yellow powder. Repeated attempts to crystallize it failed to separate it into pure constituents, so the solids were heated with water for several days, then extracted with dilute potassium hydroxide. The residue contained no halogen, and after one recrystallization melted at 157 to 160°. It was triphenylcarbinol. Upon acidification the alkali solution yielded tribromophenol. It seems likely that the original organic product was triphenylmethyl tribromophenyl ether and that the following reaction occurred

$$C_6H_2Br_3OAg + (C_6H_5)_3C \longrightarrow C_6H_2Br_3OC(C_6H_5)_3 + Ag$$
$$C_6H_2Br_3OC(C_6H_5)_3 + H_2O \longrightarrow C_6H_2Br_3OH + (C_6H_5)_3COH$$

**Reduction of Silver Salts by Phenol.**—A series of experiments was made in which 5 g. of the silver salt of tribromophenol was covered with dry benzene, varying amounts of phenol added, and the mixture heated in a water-bath for two hours. No blue color developed, but instead the benzene became orange-colored, and a gray solid was left.

The solid was filtered, extracted with sodium thiosulfate to remove silver bromide, then treated with dilute nitric acid, from which the silver was precipitated as silver chloride.

The benzene solution was evaporated under reduced pressure and the residue extracted with alcohol. The portion insoluble in alcohol resembled the amorphous oxide, but was more soluble in ether.

The alcohol extract was concentrated to 25 cc. and diluted to 300 cc. with water, precipitating tribromophenol. The water solution, upon treatment with bromine water, gave a precipitate of tribromophenol, indicating a small amount of unchanged phenol.

Carius bromine analyses were run on four samples of the amorphous ether-soluble material. Molecular weight determinations in benzene showed no appreciable depression. The yields of the various products were roughly determined.

| | | | | | | |
|---|---|---|---|---|---|---|
| Phenol used, g. | 0 | 0.2 | 0.6 | 1.3 | 1.4 | 2.0 |
| Ag recovered, g. | 0 | 0.3 | ... | 0.75 | ... | 0.8 |
| AgBr recovered, g. | 2.1 | 1.5 | ... | 0.95 | ... | 0.8 |
| Tribromophenol recov., g. | 0 | 1.2 | ... | 2.2 | ... | 3.0 |
| Br in amorphous oxide, % | 64.0 | ... | 55.7 | 34.0 | 37.8 | ... |

**Iodination of Aniline.**—This reaction was carried out in several concentrations with the same results. The following is a typical experiment. Ten grams of the anhydrous potassium salt of trichlorophenol[10] was dissolved by gentle heating in 40 cc. of dry aniline. Eleven grams (two equivalents) of iodine was added during five minutes. The mixture was heated overnight on the steam-bath, leaving a pale reddish solution with a white precipitate; 100 cc. of water was added, then 50 cc. of 2 *N* potassium hydroxide solution. The mixture was then shaken well and steam distilled. The aniline came over much more rapidly than the *p*-iodoaniline; as soon as any sign of solidification was observed in the condenser, the receiver was changed. The solid distillate was recrystallized from alcohol. It melted at 62.5 to 63°. This was not changed by twelve recrystallizations. The original product weighed 8 g.; there was obviously more in solution in the aniline.

The residue in the flask was a pale reddish solution. It was acidified; the precipitated trichlorophenol after one recrystallization weighed 8.3 g., 95% of the theoretical quantity.

The identity of the *p*-iodoaniline was established by preparing its acetyl derivative, m. p. 183.5°, and by mixed melting points with known samples prepared both from *p*-nitroiodobenzene, and from acetanilide by the action of iodine monochloride.

To make sure that the halogen was all iodine, the following analyses were made on samples recrystallized only twice, and on samples recrystallized twelve times.

*Anal.* (Carius). Calcd. for $C_6H_6IN$: I, 57.96. Found: I, 57.84, 57.66, 57.72, 57.96, 57.72. The silver iodide was converted to chloride; ratio of AgCl to AgI, calcd. 0.6105. Found: 0.6090, 0.6119, 0.6111, 0.6124.

**Acetonyl Ethers of Trihalogenated Phenols.**—The general procedure was to dissolve 5 g. of the sodium salt of a trihalogenated phenol in 50 cc. of dry acetone. One equiva-

[10] Hunter and Seyfried, THIS JOURNAL, **43**, 154 (1921).

lent of ordinary phenol was then added (in one case dimethylaniline was used), then one equivalent of iodine. The solution was heated under a reflux condenser for one hour. The acetone was then evaporated, and the residue extracted with one normal sodium hydroxide. The insoluble part was washed with water and recrystallized from alcohol and water. In general, a 40 to 75% yield of the acetonyl ether was obtained, and about half of the original trihalogenated phenol was recovered. After the latter had been precipitated by acidifying the solution, evaporation left a brownish tar, mostly phenol but containing a small amount of iodophenol.

The acetonyl ethers were pure after two or three recrystallizations. Their constitution was established by analysis and by preparing chloroacetone by the method of Fritsch[11] and reacting this with the sodium salts of trichlorophenol and tribromophenol. This reaction took place rapidly by warming the two reagents together without a solvent. Acetonyl ether of tribromoresorcinol monomethyl ether, m. p. 83°.

*Anal.* (Carius). Calcd. for $C_{10}H_9O_3Br_3$: Br, 57.54. Found: Br, 57.81, 57.66. *Mol. wt.* Calcd.: 417. Found: 381. Zeisel methoxyl, Calcd.: 7.43. Found: 7.37, 7.54, 7.19.

Acetonyl ether of trichlorophenol, m. p. 75°. *Mol. wt.* Calcd.: 253.5. Found: 258, 253. Acetonyl ether of tribromophenol, m. p. 111.5°. *Anal.* (Carius). Calcd. for $C_9H_7O_2Br_3$: Br, 62.00. Found: Br, 62.37, 62.56. Acetonyl ether of triiodophenol, m. p. 131.5°. *Anal.* (Carius). Calcd. for $C_9H_7O_2I_2$: I, 72.13. Found: I, 72.03, 71.92.

To make sure that the strong alkali used in recovering the ethers had not caused their formation from some other substances, the procedure was modified in one experiment by pouring the acetone solution into a liter of cold water, filtering, and recrystallizing fractionally from water and alcohol, in which the acetonyl ether was less soluble. No difference was noted.

In order to learn how little phenol was capable of preventing the formation of amorphous oxide, two reactions were carried out, each using 1.41 g. of sodium tribromophenolate in 15 cc. of acetone and 0.51 g. of iodine (four millimoles of each), but in the first only two millimoles of phenol, and in the second one millimole of phenol were used.

In both solutions the iodine disappeared completely overnight. Upon dilution with alcohol, no precipitate formed in the one in which half an equivalent had been used. A slight precipitate of amorphous oxide formed in the other.

## Summary

1. Various phenols and amines prevent the normal decomposition of trihalogenated phenol salts.

2. The presence of these reagents in the reaction of iodine upon alkali trihalogenophenolates results in iodination of the inhibiting reagent, excepting when the solvent is acetone, in which case the acetone is iodinated, producing finally the acetonyl ether of the trihalogenated phenol.

MINNEAPOLIS, MINNESOTA

[11] Fritsch, *Ber.*, **26**, 597 (1893).

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

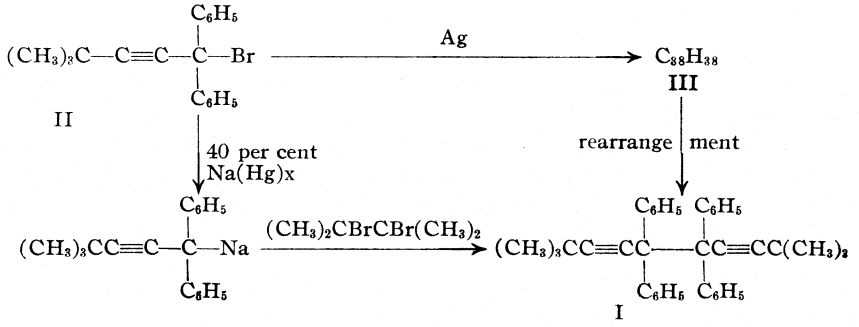
# THE REARRANGEMENT OF CERTAIN POLY-INES. THE STRUCTURE OF THE PRODUCT OBTAINED BY THE REARRANGEMENT OF TETRAPHENYLDI-TERTIARY-BUTYLETHINYLETHANE

BY D. ALTHAUSEN AND C. S. MARVEL

RECEIVED OCTOBER 22, 1931 PUBLISHED MARCH 5, 1932

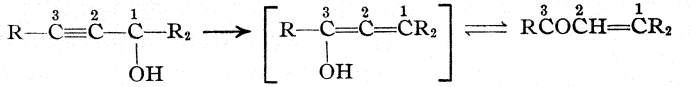
During the last few years a number of hexa-substituted ethanes containing acetylenic groups have been prepared and characterized in this Laboratory.[1] It has been observed that most of these compounds are unstable toward heat and under its influence they isomerize to give more stable hydrocarbons. Since this rearrangement seems to be characteristic of the type of poly-ine hydrocarbon which we have been studying, it has become important to investigate the structure of the rearranged compounds. The present communication describes some observations which have been made on the structure of the hydrocarbon which was formed by the rearrangement of symmetrical tetraphenyldi-*tert.*-butylethinylethane (I).

The first attempt[1c] to prepare tetraphenyldi-*tert.*-butylethinylethane (I) by the action of silver on diphenyl-*tert.*-butylethinylbromomethane (II) gave a hydrocarbon, $C_{38}H_{38}$ (III). However, this compound did not have the reactions that would be expected of the hexa-substituted ethane which was sought. More recently the true ethane (I) was prepared by a different series of reactions.[1h] The ethane was quite unstable and very quickly rearranged to produce the same isomeric hydrocarbon, $C_{38}H_{38}$, which had been obtained in the earlier work.



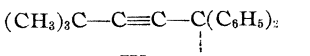

[1] The papers in this field are as follows: (a) Gray with Marvel, THIS JOURNAL, **47**, 2796 (1925); (b) Salzberg with Marvel, *ibid.*, **50**, 1737 (1928); (c) Salzberg and Marvel, *ibid.*, **50**, 2840 (1928); (d) Rossander and Marvel, *ibid.*, **51**, 932 (1929); (e) Gillespie and Marvel, *ibid.*, **52**, 3368 (1930); (f) Ozanne and Marvel, *ibid.*, **52**, 5267 (1930); (g) Davis and Marvel, *ibid.*, **53**, 3840 (1931); (h) Stampfli and Marvel, *ibid.*, **53**, 4057 (1931).

In searching for a plausible formula for the rearranged compound it occurred to us that the rearrangement of these ethanes might be related to the rearrangement of the acetylenic carbinols which has been studied by Meyer and Schuster.[2] This rearrangement is illustrated by the following formulas. The same type of rearrangement has also been observed in

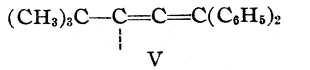


many olefinic derivatives and the shift of a group from carbon atom 1 to carbon atom 3 in such a system is not unusual.

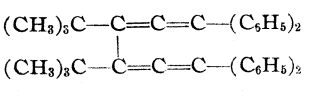
In order to have some basis for the investigation of the structure of the hydrocarbon $C_{38}H_{38}$ (III) it was assumed that the rearrangement of the ethane (I) proceeded through the stage of the free radical diphenyl-*tert.*-butylethinylmethyl (IV). This free radical would also be the first product of the action of silver on the bromide (II). If this free radical (IV) undergoes a rearrangement similar to the Meyer and Schuster rearrangement, the allene free radical (V) should result.



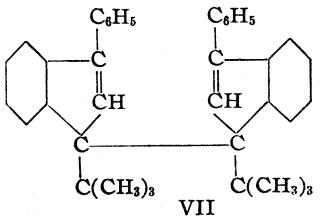
IV



V



VI



VII

The recombination of two free radicals of structure V would produce the double allene molecule indicated in formula VI. For a considerable time it was believed that this formula represented the structure of the rearranged hydrocarbon under investigation. However, the final rearrangement to a di-indene derivative was indicated by the reactions of the product. This rearrangement of a phenylallene to an indene has been amply demonstrated by the work of Vorländer and his co-workers,[3] Kohler,[4] Hurd and Webb[5] and Ziegler and Sauermilch.[6]

The reactions of the hydrocarbon, $C_{38}H_{38}$, which must be explained are the following: (1) oxidation by ozone to yield trimethylacetic acid, oxalic acid and phthalic acid besides other products which are tars; (2)

[2] Meyer and Schuster, *Ber.*, **55**, 819 (1922).

[3] Vorländer and co-workers, *ibid.*, **39**, 1024 (1906); **56**, 1122 (1923).

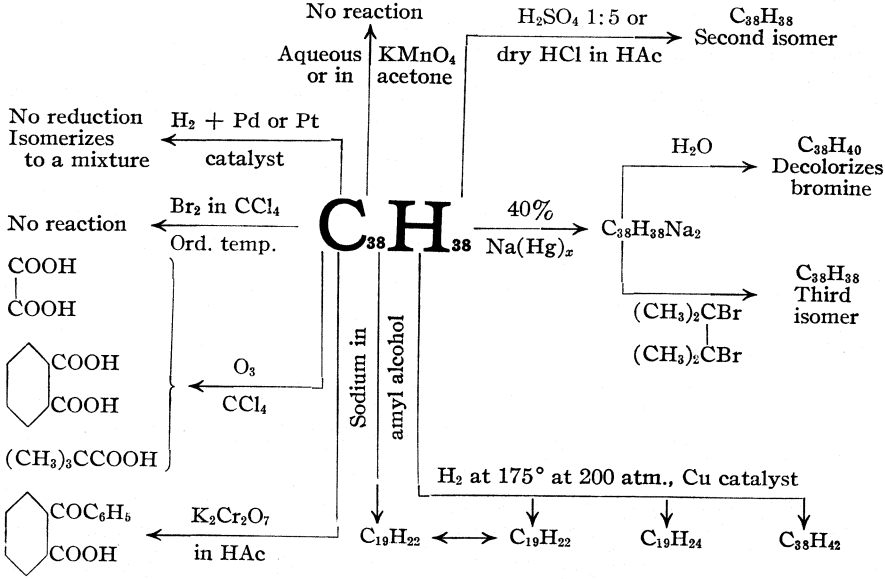
[4] Kohler, *Am. Chem. J.*, **40**, 217 (1908).

[5] Hurd and Webb, THIS JOURNAL, **49**, 546 (1927).

[6] Ziegler and Sauermilch, *Ber.*, **63**, 1851 (1930).

oxidation with potassium dichromate in acetic acid to yield *o*-benzoylbenzoic acid; (3) failure to oxidize with an aqueous alkaline potassium permanganate solution or an acetone solution of potassium permanganate; (4) failure to add bromine on treatment with bromine in carbon tetrachloride; (5) failure to reduce with hydrogen under slight pressure in the presence of platinum-oxide platinum black[7] or palladium-oxide palladium black;[8] (6 )reduction with hydrogen over a copper chromite catalyst at 175° under a pressure of 200 atmospheres to give three hydrocarbons, $C_{19}H_{22}$, $C_{19}H_{24}$ and $C_{38}H_{42}$;[9] (7) reduction with sodium and amyl alcohol to give a hydrocarbon, $C_{19}H_{22}$, which is identical with the product of this composition obtained in the high pressure reduction; (8) a reaction with 40% sodium amalgam to give a red metal alkyl which is not a cleavage product; (9) rearrangement to a more stable isomer by heating the solution in acetic acid with hydrogen chloride or sulfuric acid.

These facts are summarized in the chart.



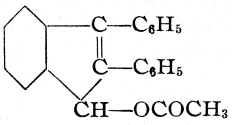

The di-indene formula which has been proposed above will account for all of these reactions in a satisfactory fashion. The ozonization of the product is very difficult to control and the benzene rings seem to be attacked almost as readily as the indene double bonds. The trimethyl-

[7] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

[8] Shriner and Adams, *ibid.*, **46**, 1683 (1924).

[9] The reduction of the hydrocarbon at higher pressures was carried out by Professor Homer Adkins and Mr. Ralph Connor at the University of Wisconsin. We take this opportunity to express our deep appreciation for their kindness in aiding us in this investigation.

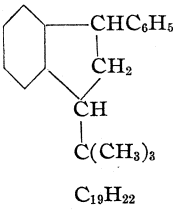
acetic acid and oxalic acid are formed from the ozonide in which the aromatic rings are attacked. The phthalic acid is formed by an opening of the indene ring and more extensive oxidation of the material. It is never present in the oxidation products in very large amounts. The oxidation with potassium dichromate in acetic acid to yield *o*-benzoylbenzoic acid is in good agreement with the results which Kohler[4] has obtained in the oxidation of 1,2,3-triphenylindene to *o*-dibenzoylbenzene. The stability of the di-indene toward potassium permanganate is in agreement with the observation of Kohler[4] that 1,2,3-triphenyl-1-ethylindene is stable toward potassium permanganate in acetone solution and that of Thiele[10] that compound (A) is not attacked by aqueous alkaline potassium permanganate.



A

The failure of the hydrocarbon to add bromine in cold carbon tetrachloride is not unusual. The phenylindenes[4] have to be heated with bromine in order to get a reaction to occur. The failure of the di-indene to reduce when treated with hydrogen in the presence of platinum and palladium catalysts is more surprising but Schlenk and Bergmann[11] have made similar observations on a compound which seems to be related in structure.

The three hydrocarbons, $C_{19}H_{22}$, $C_{19}H_{24}$ and $C_{38}H_{42}$, which have been obtained by the high pressure reduction over copper chromite catalyst, are probably the following compounds.



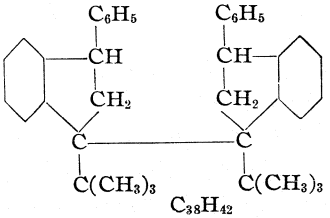
$C_{19}H_{22}$

VIII

$(CH_3)_3CCH_2CH_2CH(C_6H_5)_2$

$C_{19}H_{24}$

IX



$C_{38}H_{42}$

X

The main product of the reduction is 1-phenyl-3-*tert.*-butyldihydro-indene (VIII) which is formed by the cleavage of the bond between the two indene nuclei and then hydrogenation of the remaining indene molecules. The cleavage of the molecule at this point is not surprising. Kohler[4] has shown that silver reacts with 3-bromo-1,2,3-triphenylindene to give the free radical 1,2,3-triphenylindyl rather than the di-indene molecule. The linkage between the two indene nuclei in formula VII might be expected to be of the type which is easily broken. The hydrocarbon $C_{38}H_{42}$ which was isolated in small amounts from the reduction products is undoubtedly represented by formula X and came from reduction of the two indene rings without cleavage. The hydrocarbon $C_{19}H_{24}$ was also

[10] Thiele and Rugglis, *Ann.*, **393**, 61 (1912).

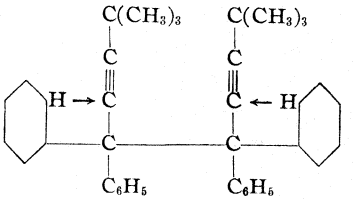
[11] W. Schlenk and Ernst Bergmann, *ibid.*, **463**, 252 (1928)

isolated in small amounts. Oxidation of this hydrocarbon gave benzophenone. Since the same hydrocarbon was obtained by the catalytic reduction of diphenyl-*tert.*-butylethinylcarbinol with hydrogen and palladium-oxide palladium black,[8] it must have been 1,1-diphenyl-4,4-dimethylpentane produced by cleavage of the dihydro-indene derivative (VIII) under the conditions of the reduction. This reaction is unusual but there seems to be no other explanation of the formation of the open-chain derivative. Reduction of the original di-indene with sodium and amyl alcohol results in a cleavage of the molecule to produce 1-phenyl-3-*tert.*-butyldihydro-indene (VIII).

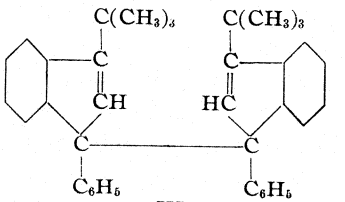
Forty per cent. sodium amalgam might be expected to cleave a di-indene molecule of the type (VII) which has been postulated. However, molecular weights of the products which were obtained from the metal derivative showed that no cleavage had occurred. Treatment of the sodium derivative with water produced a hydrocarbon $C_{38}H_{40}$ or a dihydro derivative of the original substance. This substance was unsaturated toward bromine in carbon tetrachloride but no definite bromination product was isolated. When the sodium derivative of the di-indene was treated with tetramethylethylene bromide another isomer of $C_{38}H_{38}$ was produced. It is as yet impossible to assign definite structures to either of these new hydrocarbons.

The rearrangement of the original di-indene hydrocarbon $C_{38}H_{38}$ (VII) to produce an isomer when its acetic acid solution is heated with either hydrochloric acid or sulfuric acid is not so readily accounted for. There are possible explanations. The new compound may be a geometric isomer of the original. Formula VII permits two geometrical forms. However, the rearranged product is much more stable to oxidation and reduction than is the original di-indene. The mere change in geometrical configuration might produce this stabilization. Another suggestion is that a truxane type of molecule is formed by the two indene residues combining through the double bonds. Steric considerations make this seem unlikely.

An alternate formula (XI) for the di-indene will explain the reactions of this hydrocarbon. In it the positions of two phenyls and the tertiary butyl groups are interchanged. Its formation could be accounted for by a simple shift of the hydrogen atoms and ring closure in the original tetraphenyl di-*tert.*-butylethinylethane.



I



XI

This formula is not favored at the present time. The evidence that a free radical is formed when silver reacts with the bromide[1c] seems quite conclusive. If the free radical is an intermediate in the production of the di-indene, formula VI seems the more likely.

## Experimental

**Bis-(1-phenyl-3-*tert.*-butylindyl).**—Most of the hydrocarbon used in this work was prepared from diphenyl-*tert.*-butylethinylbromomethane by the action of silver[1c] although some material was prepared by the rearrangement of tetraphenyldi-*tert.*-butylethinylethane.[1h] It was found that the di-indene could be purified by recrystallization from glacial acetic acid or by dissolving it in the least amount of petroleum ether (b. p. 65–110°) and adding two volumes of ethyl alcohol. The hydrocarbon then melted sharply at 150–151°.

**Oxidation of the Di-indene with Ozone.**—Some thirty experiments on the ozonization of this hydrocarbon were performed. The principal conditions which were changed were amount of material, volume and nature of the solvent and the time of treatment. Some experiments were made with ozonized air but most of the important results were obtained using ozonized oxygen.

The general procedure used in the ozone oxidation may be briefly summarized. The hydrocarbon was dissolved in 200–300 cc. of solvent and ozonized oxygen was passed through the solution at the rate of 0.4 liter per minute. The ozonide thus formed was decomposed with water in the presence of either oxidizing or reducing agents. Some typical runs are listed in Table I. Many of these experiments were repeated several times in order to check the results with certainty.

TABLE I

OZONIZATION OF THE DI-INDENE

| Run | Hydrocarbon, g. | Solvent | Time of ozonization, hrs. | Reagents used to decompose ozonide | Products isolated |
|---|---|---|---|---|---|
| 5 | 2.9 | Carbon tetrachloride | 3 | $H_2O + H_2O_2$ | Unchanged hydrocarbon |
| 9 | 2.2 | Petroleum ether | 6 | $H_2O + H_2O_2$ | Unchanged hydrocarbon |
| 10 | 1.4 | Petroleum ether | 8 | $H_2O + H_2O_2$ | Unchanged hydrocarbon |
| 2 | 3.0 | Carbon tetrachloride | 10 | $H_2O + H_2O_2$ | Phthalic acid, oxalic acid |
| 11 | 1.5 | Petroleum ether | 16 | $H_2O$, Zn + $CH_3CO_2H$ | Yellow oil |
| 4 | 2.9 | Carbon tetrachloride | 18 | $H_2O + H_2O_2$ | Phthalic acid, oxalic acid |
| 1 | 2 | Carbon tetrachloride | 18.5 | $H_2O + H_2O_2$ | Phthalic acid, oxalic acid |
| 3 | 8.5 | Carbon tetrachloride | 21.5 | $H_2O + H_2O_2$ | Phthalic acid, trimethylacetic acid, oxalic acid |
| 7 | 5 | Petroleum ether | 23.5 | $H_2O + H_2O_2$ | Trimethylacetic acid, oxalic acid |
| 8 | 2 | Carbon tetrachloride | 25 | $H_2O + H_2O_2$ | Phthalic acid, oxalic acid |
| 6 | 2.4 | Carbon tetrachloride | 30 | $H_2O + H_2O_2$ | Completely burned |

The carbon tetrachloride was always carefully dried over calcium chloride and redistilled before using in these experiments. The petroleum ether was treated with 10% potassium permanganate several times, washed with concentrated sulfuric acid, then with water, dried over fused calcium chloride and then sodium and redistilled. The portion boiling at 60–90° was used.

After ozonization the reaction mixture was poured into the media used for decomposition and stirred. Then the aqueous layer was made alkaline by the addition of 10% sodium hydroxide solution. This always produced a red color in the water

layer. After separating the two layers the aqueous portion was evaporated to about 50 cc., filtered, cooled in ice and carefully acidified. A very small precipitate was usually obtained. This amounted to only 0.16 to 0.24 g. in various runs. It was identified as phthalic acid by recrystallization from 50% alcohol until it melted at 190–196°. The neutral equivalent confirmed the identification.

*Neutral equivalent.* Subs., 0.0140: 14.3 cc. of 0.01153 *N* NaOH. Calcd. for $C_6H_4(COOH)_2$: 83. Found: 85.

The solution after the removal of the water-insoluble portion was extracted with ether. The aqueous layer was tested for oxalic acid by precipitation of the calcium salt. The calcium salt was identified by drying it and titrating it with standard potassium permanganate solution. Oxalic acid was identified in all runs which were exposed to ozone for more than ten hours.

The ether extract was shaken with water to which just enough 5% sodium hydroxide was added to keep the solution alkaline to phenolphthalein. The ether layer was then discarded and the aqueous layer was evaporated to dryness. The remaining salt was washed with ether a few times and dissolved in 50 cc. of 95% alcohol and filtered. The filtrate was evaporated to dryness and the weight of the salt noted. This salt was then treated with *p*-bromophenacyl bromide according to the directions of Judefind and Reid.[12] After three crystallizations from alcohol the ester thus obtained melted at 76–77° and was shown to be identical with an authentic specimen of the ester prepared from trimethylacetic acid as described by Powell.[13] A sample of our ester was analyzed to make sure of its composition.

*Anal.* (Parr bomb). Subs., 0.1960: 6.71 cc. of 0.09688 *N* $AgNO_3$. Calcd. for $C_{13}H_{15}O_3Br$: Br, 26.75. Found: Br, 26.53.

The identification of trimethylacetic acid was carried out only in runs 3 and 7 (Table I). Its odor was noticeable in the other experiments.

When the ozonization experiments were first undertaken, it was thought that the hydrocarbon might be the di-allene (VI) which should yield dipivaloyl, carbon dioxide and benzophenone on ozonization. Experiments showed that dipivaloyl[14] was converted to trimethylacetic acid under the conditions used in the ozonization and decomposition of the ozonide. Benzophenone could be partially recovered when treated with ozone and then with hydrogen peroxide. No benzophenone was detected in the products of ozonization of the hydrocarbon in spite of every effort to find it.

**Oxidation with Potassium Dichromate in Acetic Acid.**—To a solution of 5.23 g. of the hydrocarbon in 100 cc. of glacial acetic acid was added 25 g. of potassium dichromate. The solution was boiled under a reflux condenser for about ten hours, then poured into 200 cc. of water, cooled and filtered. The precipitate and the aqueous layer were separately extracted with ether. The ether extracts were combined and extracted with sodium carbonate solution. The ether solution was evaporated and gave oily material which did not contain benzophenone. The aqueous alkaline solution was acidified with hydrochloric acid and gave 1.12 g. of water-insoluble acid. Four recrystallizations from 50% alcohol gave a product which melted at 90°. After thorough drying this material melted at 127–128°. These melting points agreed with those of hydrated and anhydrous *o*-benzoylbenzoic acid. A mixed melting point with known *o*-benzoylbenzoic acid showed no depression in melting point. The neutral equivalent furnished further evidence of this structure.

[12] Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

[13] Powell, *ibid.*, **53**, 1172 (1931).

[14] This material used was furnished by Dr. S. M. McElvain of the University of Wisconsin.

*Neutral equivalent.* Subs., 0.2413: 24.85 cc. of 0.04315 *N* NaOH. Calcd. for $C_{13}H_{10}O_2$: neut. equiv., 226. Found: 225.

**Other Experiments on Oxidation.**—The hydrocarbon was oxidized with hot nitric acid in glacial acetic acid but no definite products could be isolated from the yellow resinous mass obtained by diluting the reaction mixture with water.

Attempts to oxidize the hydrocarbon with potassium permanganate in water and in acetone solutions were unsuccessful and the original material was recovered. In one typical experiment 2 g. of hydrocarbon in 150 cc. of acetone was treated with 20 g. of potassium permanganate and the mixture was refluxed for twelve hours. A 90% recovery of this hydrocarbon was obtained.

The hydrocarbon was not attacked by hydrogen peroxide in acid or alkaline solution at ordinary temperatures. No acidic compounds were obtained by fusion of the hydrocarbon with dry sodium hydroxide.

**Attempt to Brominate the Di-indene Derivative.**—To a solution of 0.1 g. of the hydrocarbon in 10 cc. of carbon tetrachloride was added 10 drops of a 5% solution of bromine in carbon tetrachloride. The color of the bromine had not disappeared after ten hours and no brominated derivative was obtained.

**Attempted Reduction with Hydrogen and Platinum or Palladium Catalysts.**—Several attempts were made to hydrogenate the hydrocarbon using hydrogen and platinum[7] and palladium[8] catalysts. At ordinary temperature and at 60–70° in either ethyl acetate or acetic acid solution, no hydrogenation occurred with these catalysts with hydrogen at 40 to 50 pounds' pressure in a Burgess–Parr hydrogenation apparatus.

**Hydrogenation of the Di-indene Derivative at High Pressures.**[9]—Ten grams of the hydrocarbon in methylcyclohexane solution was treated with hydrogen at 175° and 3000 pounds' pressure in the presence of a copper chromite catalyst. When no further hydrogen was absorbed, the catalyst was removed from the solution and the solvent was evaporated. A salve-like mixture of hydrocarbons remained. This residue weighed 8.5 g.

This sample was placed in a distilling bulb and heated under a pressure of 1 mm. to 185–195°. A small amount of distillate, 0.76 g., was obtained. This product boiled at 122–127° at 1 mm., $d_4^{20}$ 0.9520; $n_D^{20}$ 1.5411; $M_D$ calcd. for $C_{19}H_{24}$ (1,1-diphenyl-4,4-dimethylpentane), 82.76. Found: 83.18.

*Anal.* Subs., 0.1262: $CO_2$, 0.4180; $H_2O$, 0.1074. Calcd. for $C_{19}H_{24}$: C, 90.40; H, 9.60. Found: C, 90.33; H, 9.52.

This liquid hydrocarbon did not absorb bromine in carbon tetrachloride. It is identical in properties with the hydrocarbon which was obtained by the reduction of diphenyl-*tert.*-butylethinylcarbinol with hydrogen over a palladium catalyst.

The solid which remained in the distilling flask was a mixture of hydrocarbons. After twenty-four recrystallizations from acetone a pure sample was isolated. This product weighed 0.09 g. and melted at 181–182°.

*Anal.* Subs., 2.627, 2.612 mg.: $CO_2$, 8.771, 8.746 mg.; $H_2O$, 1.903, 1.916 mg. Calcd. for $C_{19}H_{22}$: C, 91.13; H, 8.87. Found: C, 91.06, 91.32; H, 8.11, 8.21.[15] *Mol. wt.* (Rast). Subs., 0.00425; camphor, 0.01685; $\Delta t$, 39.7°. Calcd. for $C_{19}H_{22}$: mol. wt., 250. Found: mol. wt., 254.

The residue from the mother liquor of the recrystallizations was crystallized from methyl alcohol and yielded 0.0875 g. of a second hydrocarbon, m. p. 132–133°.

*Anal.* Subs., 2.880, 2.359 mg.: $CO_2$, 9.651, 7.912 mg.; $H_2O$, 2.067, 1.702 mg.

[15] We are indebted to Dr. W. H. Carothers and Mr. S. B. Kuykendall of the du Pont Experimental Station for the microanalyses reported in this paper.

Calcd. for $C_{38}H_{42}$: C, 91.50; H, 8.50. Found: C, 91.39, 91.47; H, 8.03, 8.02. *Mol. wt.* (Rast) Subs., 0.0058 g.; camphor, 0.0160; $\Delta t$, 29.87°. Calcd. for $C_{38}H_{42}$: mol. wt., 498. Found: mol. wt., 480.

This compound did not add bromine in carbon tetrachloride solution and was waxy in appearance.

An analysis on the crude mixture of hydrocarbons before the separation of these two compounds showed that the mixture had essentially the composition $C_{19}H_{21-22}$.

**Reduction of the Di-indene Derivative with Sodium and Amyl Alcohol.**—To a solution of 1.8 g. of the di-indene derivative in 100 cc. of hot amyl alcohol was added 15 g. of sodium in small pieces. When the sodium had dissolved, the mixture was cooled and treated with water. The alcohol layer was separated and washed several times with water. The alcohol was then removed under reduced pressure and the residue was crystallized from acetone. The product melted at 180–181° and by means of a mixed melting point determination was shown to be identical with the hydrocarbon $C_{19}H_{22}$ obtained from the high pressure reduction of the di-indene.

A solution of 0.89 g. of this hydrocarbon in 25 cc. of glacial acetic acid was boiled with 5 g. of potassium dichromate for about ten hours. The material (0.69 g.) was recovered unchanged.

**Reaction of the Di-indene Derivative with Sodium Amalgam.**[16]—A solution of 4 g. of the hydrocarbon in 100 cc. of dry ether was shaken with 5 cc. of 40% sodium amalgam in an atmosphere of nitrogen. A deep red color soon developed. After about thirty-six hours, the amalgam was frozen and the ether solution of the sodium derivative was transferred in an atmosphere of nitrogen to another flask. Then a 10% solution of tetramethylethylene dibromide was added gradually until the red color of the solution disappeared and a few cc. excess was then added. The ether solution was filtered and evaporated under reduced pressure. A little petroleum ether (b. p. 65–110°) was added to the residue and the mixture was cooled with solid carbon dioxide. Crystals separated and were collected on a Büchner funnel and washed with cold petroleum ether. There was thus obtained 1.34 g. of a white solid, m. p. 178.5–180°. Recrystallization from petroleum ether gave 1.02 g. of product, m. p. 179.3–180.3°.

*Anal.* Subs., 0.1706, 0.1725: $CO_2$, 0.5761, 0.5838; $H_2O$, 0.1188, 0.1202. Calcd. for $C_{38}H_{38}$: C, 92.31; H, 7.69. Found: C, 92.10, 92.30; H, 7.74, 7.74. *Mol. wt.*, (Rast) Subs., 0.0074; camphor, 0.0172; $\Delta t$, 36.9°. Calcd. for $C_{38}H_{38}$: mol. wt., 494. Found: mol. wt., 465.

When the sodium derivative was prepared in a similar fashion and then treated with dry carbon dioxide, no acid could be obtained from the reaction mixture. The sodium derivative with water gave a hydrocarbon $C_{38}H_{40}$.[1h]

**Reactions of the Hydrocarbon $C_{38}H_{40}$.**—The hydrocarbon $C_{38}H_{40}$ was prepared as previously described.[1h] It decolorized bromine in carbon tetrachloride rather rapidly but no pure sample of brominated product could be obtained from the reaction mixture. When ozonized the molecule suffered rather complete cleavage and no products of significance could be isolated. It did not hydrogenate when treated with hydrogen in the presence of platinum-oxide platinum black. It did reduce when treated with sodium and alcohol.

To a solution of one gram of the hydrocarbon, $C_{38}H_{40}$, in 50 cc. of absolute alcohol, was added 7 g. of sodium cut in small pieces. When the sodium had dissolved, the reaction mixture was flooded with water and extracted with ether. On concentration of the ether a hydrocarbon crystallized and was collected on a filter. After recrystallization from ether it melted at 181–182°. It was not identical with the hydrocarbon

[16] The reactions of this sodium derivative were studied by Dr. J. Gail Stampfli.

$C_{19}H_{22}$ previously described in this paper which melted at the same temperature. This was established by mixed melting point determinations as well as by the analysis and molecular weight determinations.

*Anal.* Subs., 0.1366: $CO_2$, 0.4576; $H_2O$, 0.1034. Calcd. for $C_{38}H_{42}$: C, 91.50, H, 8.50. Found: C, 91.36; H, 8.49. *Mol. wt.* (Rast). Subs., 0.00375; camphor; 0.01885; $\Delta t$, 15.84°. Calcd. for $C_{38}H_{42}$: mol. wt., 498. Found: mol. wt., 498.

**Rearrangement of the Di-indene Derivative by Heating an Acetic Acid Solution Containing Dry Hydrogen Chloride.**—Heating the solution of the di-indene derivative in acetic acid for as long as thirty-three hours did not cause it to isomerize. However, heating a solution of 2.4 g. of the hydrocarbon with 1 cc. of concentrated sulfuric acid in 50 cc. of glacial acetic acid for one hour gave evidence of some change, as the product melted over a wide range when isolated from the mixture. By continuing the heating for several hours an isomeric hydrocarbon melting at 166–168° was obtained. A pure sample was obtained by the use of hydrogen chloride in place of the sulfuric acid.

A solution of 7 g. of the di-indene derivative in 100 cc. of glacial acetic acid was boiled for forty-eight hours. A continuous stream of dry hydrogen chloride was passed through the solution during this time. On evaporating the solution and recrystallizing the residue from alcohol there was obtained 4.2 g. of a hydrocarbon which melted at 173–174°.

*Anal.* Subs., 0.1528: $CO_2$, 0.5109; $H_2O$, 0.1073. Calcd. for $C_{38}H_{38}$: C, 92.31; H, 7.69. Found: C, 91.20; H, 7.86. *Mol. wt.* (Rast) Subs., 0.0037; camphor, 0.0180; $\Delta t$, 18.45°. Calcd. for $C_{38}H_{38}$: mol. wt., 494. Found: mol. wt., 441.

This isomer of $C_{38}H_{38}$ was recovered unchanged when a sample was boiled with an acetic acid solution of potassium dichromate. It could not be further reduced with sodium and hot amyl alcohol.

**1,1-Diphenyl-4,4-dimethylpentane.**—This hydrocarbon, which has previously been described as a reduction product of the di-indene derivative when hydrogen and copper chromite catalyst was used, was also obtained by the reduction of diphenyl-*tert.*-butylethinylcarbinol.

To a solution of 26.4 g. of the carbinol in 100 cc. of glacial acetic acid was added 0.5 g. of palladous oxide catalyst.[8] The solution was reduced with hydrogen in a Burgess–Parr hydrogenation apparatus. Reduction was complete in one hour. The solution was poured into water and extracted with ether. The ether layer was washed with sodium carbonate solution, dried and distilled. After the ether was removed at ordinary temperatures, the remaining oil boiled at 114–116° (0.65–0.70 mm.). The yield was 19 g. (75% of the theoretical amount); $n_D^{20}$ 1.5148; $d_4^{20}$ 0.9522.

*Anal.* Subs., 0.2304, $CO_2$, 0.7650; $H_2O$, 0.1968. Calcd. for $C_{19}H_{24}$: C, 90.40; H, 9.60. Found: C, 90.55; H, 9.56.

The structure of this hydrocarbon was confirmed by oxidation with chromic oxide in acetic acid solution. To a solution of 10 cc. of the hydrocarbon in 50 cc. of glacial acetic acid was added 10 g. of chromium oxide. The mixture was boiled under a reflux condenser for about five hours. Water was added and an oily substance separated. This material was dissolved in ether and extracted with aqueous alkali. No acidic substance insoluble in water was obtained by acidification of this alkaline extract. The ether was evaporated and the oil was dissolved in 2 to 3 cc. of ethyl alcohol. A few drops of phenylhydrazine were added and the mixture was heated for about one hour. The solution was cooled and after three days some crystals separated. These were filtered and recrystallized from alcohol. In this manner 0.165 g. of the phenylhydrazine of benzophenone melting at 137–138° was obtained. It was further identified by taking a mixed melting point with a known specimen of this phenylhydrazone.

## Summary

1. Various reactions of the hydrocarbon $C_{38}H_{38}$ which is obtained by the rearrangement of tetraphenyldi-*tert.*-butylethinylethane have been described.

2. All of these reactions can be explained by the postulation of a di-indene structure for the rearranged hydrocarbon.

3. The mechanism of the rearrangement of the hexasubstituted ethane to the di-indene has been discussed.


URBANA, ILLINOIS

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

# THE REDUCTION OF ACETYLENIC CARBINOLS WITH TITANIUM TRICHLORIDE

BY R. S. SWEET AND C. S. MARVEL

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The classical method of Gomberg[1] for the preparation of hexa-arylethanes does not always lead to the expected product when it is applied to the corresponding acetylene derivatives. The general method which Ziegler and Schnell[2] have developed is more reliable for producing compounds of the normal type in the acetylene series. These facts have been well established in connection with the study of the preparation and rearrangement of tetraphenyldi-*tert.*-butylethinylethane.[3]

A third general method for the preparation of aryl substituted ethanes is the reduction of aryl carbinols with vanadous, chromous or titanous salts. This method was first described by Conant and Sloan.[4] Two attempts to apply this method to the preparation of acetylenic ethanes have been recorded. Tri-*tert.*-butylethinylcarbinol gave no products which could be isolated and characterized when it was treated with vanadous chloride.[5] Wieland and Kloss[6] have reduced diphenylphenylethinylcarbinol (I) with titanium trichloride and obtained the same hydrocarbon which Moureu, Dufraisse and Houghton[7] had previously prepared by the action of iron on diphenylphenylethinylchloromethane (II). This hydrocarbon has been assumed to be *sym.*-tetraphenyldiphenylethinylethane (III).

[1] Gomberg, THIS JOURNAL, **22**, 757 (1900).

[2] Ziegler and Schnell, *Ann.*, **437**, 244 (1924).

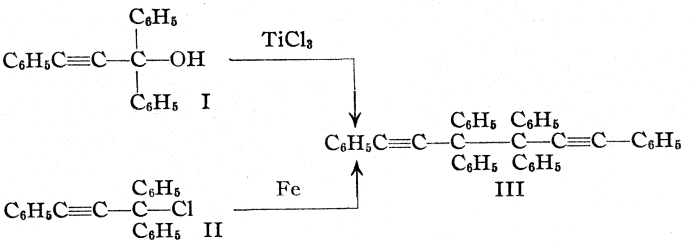
[3] (a) Salzberg and Marvel, THIS JOURNAL, **50**, 2840 (1928); (b) Stampfli and Marvel, *ibid.*, **53**, 4057 (1931); (c) Althausen and Marvel, *ibid.*, **54**, 1174 (1932).

[4] Conant and Sloan, *ibid.*, **45**, 2466 (1923).

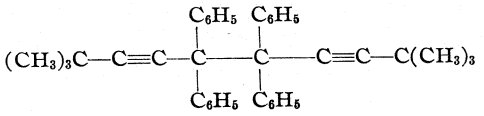
[5] Salzberg with Marvel, *ibid.*, **50**, 1737 (1928).

[6] Wieland and Kloss, *Ann.*, **470**, 217 (1929).

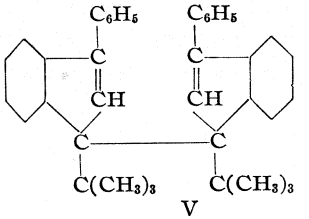
[7] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).




There is a considerable difference in the properties of this tetra-aryl diacetylenic ethane and the closely related tetraphenyldi-*tert.*-butylethinylethane (IV) which has recently been prepared and characterized.[3b] This latter compound undergoes rearrangement in solution at room temperature to give a more stable substance which has a di-indene (V) structure.[3c]




IV




V

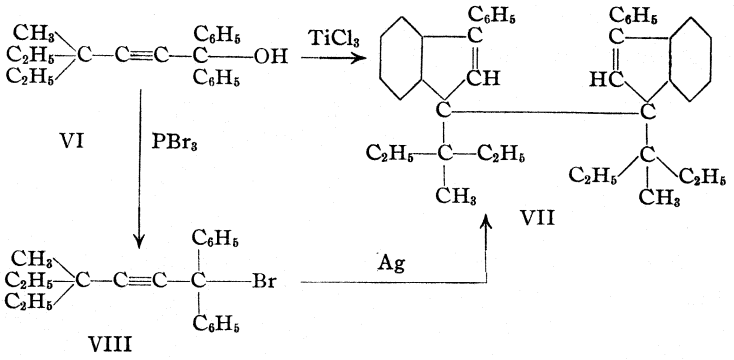
On the other hand the hydrocarbon which has been assumed to be tetraphenyldiphenylethinylethane has been found to be quite stable.

The differences in the properties of these two closely related hydrocarbons suggest that Moureu and his co-workers and Wieland and Kloss may have obtained some product other than the true ethane by their methods of preparation. It is as yet impossible to state definitely that such is the case. However, this paper will present data to show that titanium trichloride does not produce the expected hexasubstituted ethanes from some typical acetylenic carbinols.

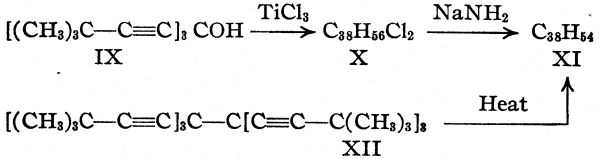
The reaction between titanium trichloride in alcoholic hydrochloric acid solution and diphenyl-*tert.*-butylethinylcarbinol proceeded rather smoothly and yielded about 25% of the theoretical amount of a hydrocarbon, $C_{38}H_{38}$. At the same time about 50% of the carbinol was converted to the unsaturated ketone $(CH_3)_3CCOCH{=}C(C_6H_5)_2$. The hydrocarbon, $C_{38}H_{38}$, was found to be identical with the di-indene derivative (V) which results from the rearrangement of tetraphenyldi-*tert.*-butylethinylethane.

Similarly titanium trichloride reduced diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol (VI) to produce a hydrocarbon, $C_{42}H_{46}$.

The same hydrocarbon was obtained by converting the carbinol to the bromide (VIII) and treating this with silver. Since these reactions are exactly analogous to those used on the *tert.*-butyl derivative, it seems logical to assume here that the hydrocarbon has the di-indene structure.




When tri-*tert.*-butylethinylcarbinol (IX) was treated with titanium trichloride, a compound containing chlorine (X) was the main product of the reaction. This chloro compound was found to correspond in composition to a di-hydrochloride of the expected hydrocarbon. When the chlorine containing compound was treated with sodamide, two molecules of hydrogen chloride were removed and a hydrocarbon (XI) was obtained. This hydrocarbon was not hexa-*tert.*-butylethinylethane (XII) but the isomeric compound which is formed when this ethane is heated.[5]




The structure of this hydrocarbon (XI) is still uncertain. It has been found to be attacked slowly by bromine in carbon tetrachloride, and by aqueous potassium permanganate solution. Its solution in glacial acetic acid does not yield colored compounds with tetranitromethane. It is not easily reduced with hydrogen in the presence of a platinum-oxide platinum black catalyst.[8] It gives colored products on treatment with 40% sodium amalgam but these have not been characterized.

The mechanism by which the diaryl monoacetylenic carbinols are converted to di-indene derivatives by the action of titanium trichloride is probably similar to that which has been suggested for the rearrangement of tetraphenyldi-*tert.*-butylethinylethane.[3c] The first step cannot be the conversion of the carbinol to the $\alpha,\beta$-unsaturated ketone under the influence of the acid reagent, because this ketone is unaffected by the titanium trichloride.

Several other acetylenic carbinols were treated with this reagent but no definite products could be obtained. Since some of these carbinols are new, their synthesis has been included in the experimental part of this paper.

[8] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

The three reduction experiments using diphenyl-*tert.*-butylethinylcarbinol, diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol and tri-*tert.*-butylethinylcarbinol are sufficient to show that titanium trichloride cannot always be relied upon to yield the expected hexasubstituted ethanes from the corresponding acetylenic carbinols. Further work is in progress on this reaction and on the structure of the hydrocarbon which has been described as tetraphenyldiphenylethinylethane in order to determine whether or not it has that structure or is of the di-indene type.

## Experimental Part

**(3-Methyl-3-ethylpentinyl-1)-diphenylcarbinol.**—In a 200-cc. three-necked, round-bottomed flask, fitted with a mechanical stirrer, a separatory funnel and a reflux condenser was placed 56 cc. of a 4.03 *N* ethylmagnesium bromide solution in ether. During a period of about twelve hours, 25 g. of 3-methyl-3-ethylpentine-1[9] was added to the well-stirred solution from the separatory funnel. To this solution was then added 36.1 g. of benzophenone dissolved in 100 cc. of dry ether over a period of about thirty hours. The mixture was well stirred during the entire reaction.

The Grignard reaction mixture was decomposed by pouring it onto about 300 g. of cracked ice and ammonium chloride solution was added to dissolve the magnesium salts. The ether layer was separated, dried over anhydrous sodium sulfate and the solvent was evaporated under ordinary pressure. The residue was distilled under reduced pressure. The carbinol came over at 154–156° (0.5 mm.). The yield was 40 g. (71% of the theoretical amount); $n_D^{20}$ 1.5626; sp. gr. $^{20}/_{20}$ 1.0256.

*Anal.* Subs., 0.2064: $CO_2$, 0.6543; $H_2O$, 0.1504. Calcd. for $C_{21}H_{24}O$: C, 86.30; H, 8.21. Found: C, 86.45; H, 8.15.

**(3-Methyl-3-ethylpentinyl-1)-diphenylbromomethane.**—A solution of 3.0466 g. of the above carbinol in 25 cc. of petroleum ether (b. p. 25–65°) was placed in a 200-cc. flask fitted with a stirrer and protected from the air with a calcium chloride tube and then cooled in an ice-bath. To the well-stirred cold solution was added over a period of one-half hour, 1 cc. of phosphorus tribromide dissolved in 10 cc. of petroleum ether. After the phosphorus tribromide has been added the mixture was stirred for a few minutes and then 100 cc. of 5% sodium bicarbonate solution was added and stirring was continued for about ten minutes. The petroleum ether solution was separated, dried over anhydrous sodium sulfate and filtered. Attempts to isolate a crystalline bromide were unsuccessful and this solution was used directly in the next preparation.

**The Hydrocarbon $C_{42}H_{46}$ from (3-Methyl-3-ethylpentinyl-1)-diphenylbromomethane and Silver.**—The petroleum ether solution of the bromide prepared as described above was transferred to a 50-cc. round-bottomed flask and the solvent was removed by evaporation under reduced pressure at ordinary temperatures. The remaining bromide was taken up in 25 cc. of anhydrous ether, the flask was flushed out with dry nitrogen, 3 g. of molecular silver was introduced and the flask was tightly stoppered. The mixture was shaken on a mechanical shaker for about forty-eight hours and then the solution was filtered, and concentrated to about 5 cc. under reduced pressure at ordinary temperatures. To the residue was added 10 cc. of absolute alcohol and dry air was drawn through the solution to further concentrate it until crystals began to appear. The solution was cooled, and the crystals were collected on a Büchner funnel. After a second crystallization from ether and alcohol there was obtained 1.4877 g. (51.5% of the theoretical amount) of a hydrocarbon, m. p. 105–106°.

[9] Davis and Marvel, THIS JOURNAL, **53**, 3840 (1931).

*Anal.* Subs., 0.1941, $CO_2$, 0.6535; $H_2O$, 0.1453. Calcd. for $C_{42}H_{46}$: C, 91.63; H, 8.36. Found: C, 91.82; H, 8.37. *Mol. wt.* (Cryoscopic in benzene). Subs., 0.1032; benzene, 21.679; $\Delta t$ (depression), 0.048°. Calcd. for $C_{42}H_{46}$: mol. wt. 550. Found: 508.

This hydrocarbon did not absorb oxygen in the air. It did not rearrange further on heating alone or on heating it in acetic acid solution containing dry hydrogen chloride. It gave a colored sodium derivative when treated with 40% sodium amalgam but no evidence of cleavage could be obtained since this sodium derivative did not produce water-insoluble acids on treatment with carbon dioxide.

The hydrocarbon was oxidized in an attempt to obtain evidence to confirm its structure as a di-indene derivative. A solution of 2.227 g. of the hydrocarbon and 12.5 g. of potassium dichromate in 50 cc. of glacial acetic acid was refluxed for about ten hours. The solution was poured into 50 cc. of water. The mixture was thoroughly extracted with ether. The ether extract was in turn extracted with 10% aqueous sodium hydroxide solution but no water-insoluble acids were removed. On evaporation the ether solution yielded a solid which was recrystallized from alcohol. There was thus obtained about 0.15 g. of solid; m. p. 135–136°.

*Anal.* (Micro) Subs., 2.390, 2.142: $CO_2$, 7.626, 6.821; $H_2O$, 1.423, 1.216. Found: C, 87.02, 86.85; H, 6.66, 6.35.[10]

The nature of this oxidation product is uncertain.

**Tri-isopropylethinylcarbinol.**—Isopropyl methyl ketone was prepared in yields of 45% of the theoretical amount from isopropylmagnesium bromide and acetic anhydride following the directions of Adams and Roll for cyclohexyl methyl ketone.[11] This ketone was converted to isopropylacetylene in yields of about 18% following essentially the method previously described for the preparation of *tert.*-butylacetylene.[12] Tri-isopropylethinylcarbinol was prepared according to the procedure described for tri-(3-ethyl-3-methylpentinyl-1)-carbinol.[13] Using 34 g. of the acetylene, 146 cc. of 3.14 *N* ethylmagnesium bromide solution in ether and 48.5 cc. of diethyl carbonate, the yield of carbinol was 17.7 g. (45% of the theoretical amount); b. p. 118–121° (2 mm.); $n_D^{20}$ 1.475; sp. gr. $^{20}/_{20}$ 0.8848.

*Anal.* Subs., 0.1530: $CO_2$, 0.4691; $H_2O$, 0.1322. Calcd. for $C_{16}H_{22}O$: C, 83.5; H, 9.56. Found: C, 83.62; H, 9.66.

Attempts to convert this carbinol to the bromide and the corresponding ethane by the usual methods gave unsatisfactory results.

**Tricyclohexylethinylcarbinol.**—Cyclohexyl methyl ketone was prepared in 56% yields from cyclohexylmagnesium bromide and acetic anhydride.[10] This in turn gave 70–80% of the theoretical amount of hexahydro-ω-chlorostyrene on treatment with phosphorus pentachloride. Cyclohexylacetylene was obtained in 46% yields from the chloro compound with powdered potassium hydroxide according to the method of Darzens and Rost.[14] The acetylene was converted to tricyclohexylethinylcarbinol by the usual process. However, this carbinol did not crystallize and decomposed on attempted distillation. Therefore, it could not be definitely characterized.

**Diphenyl-*tert.*-butylethinylcarbinol and Titanium Trichloride.**—In a 200-cc. three-necked round-bottomed flask fitted with a short reflux condenser, a mechanical stirrer

[10] The authors are indebted to Dr. W. H. Carothers and Mr. S. B. Kuykendall of the du Pont Experimental Station for this analysis.

[11] Adams and Roll, private communication.

[12] Ivitzky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

[13] Davis and Marvel, THIS JOURNAL, **53**, 3846 (1931).

[14] Darzens and Rost, *Compt. rend.*, **149**, 681 (1909).

and a separatory funnel was placed a solution of 4 g. of diphenyl-*tert.*-butylethinylcarbinol in 400 cc. of absolute alcohol. The mixture was warmed in a water-bath to 60–65°, a stirrer was started and 20 cc. of a 20% solution of titanium trichloride was added from the separatory funnel during one-half hour. The mixture was stirred about one-half hour longer, cooled, and extracted with ether. The ether layer was thoroughly washed with water and then dried over anhydrous sodium sulfate. The solution was filtered, the solvent evaporated, and the residue was crystallized from alcohol and ether. The yield was 0.9263 g. (24.7% of the theoretical amount) of a hydrocarbon melting at 150–151°. A mixture of this hydrocarbon with a sample of the di-indene obtained by the rearrangement of tetraphenyldi-*tert.*-butylethinylethane melted at the same temperature.

In another experiment 10 g. of the carbinol was treated with titanium trichloride. This gave 1.5 g. of the di-indene and 8 g. of a yellow oil which after distillation (b. p. 140° at 4 mm.) slowly crystallized. This product after recrystallization from alcohol melted at 65–66°. It gave no depression in melting point when mixed with an authentic specimen of 1,1-diphenyl-4,4-dimethylpentene-1-one-3 which had been prepared by the rearrangement of the same carbinol by treatment with acids.

**1,1-Diphenyl-4,4-dimethylpentene-1-one-3 and Titanium Trichloride.**—A solution of 5 g. of the ketone in 50 cc. of 95% alcohol was treated with 25 cc. of 20% titanium trichloride at 60° for two hours. On examining the reaction mixture 4 g. of unchanged ketone was recovered and no hydrocarbon could be detected.

**(3-Methyl-3-ethylpentinyl-1)-diphenylcarbinol and Titanium Trichloride.**—Three grams of this carbinol was treated with titanium trichloride as described above. After four recrystallizations from alcohol, the yield was 1.29 g. (44% of the theoretical amount). The product melted at 105–106° and was identical with the hydrocarbon, $C_{42}H_{46}$, previously prepared by treating (3-methyl-3-ethylpentinyl-1)-diphenylbromomethane with silver.

**Tri-*tert.*-butylethinylcarbinol and Titanium Trichloride.**—Three grams of this carbinol was treated with titanium trichloride and yielded 1.686 g. of a white crystalline compound, m. p. 175–176°, which contained chlorine.

*Anal.* (Micro) Subs., 4.513: AgCl, 2.36. Calcd. for $C_{38}H_{56}Cl_2$: Cl, 12.18. Found: Cl, 12.93.[15] *Mol. wt.* (cryoscopic in benzene). Subs., 0.3024, 0.6026; benzene, 21.679; $\Delta t$ (depression), 0.129°, 0.262°. Calcd. for $C_{38}H_{56}Cl_2$: mol. wt. 583. Found: 553, 543.

This chloro compound was boiled with 10% alcoholic potassium hydroxide solution and recovered unchanged. Sodamide removed hydrogen chloride.

In a 200-cc. three-necked round-bottomed flask fitted with a mechanical stirrer, a reflux condenser and a separatory funnel, was placed 4 g. of finely powdered sodamide suspended in 100 cc. of dry xylene. The xylene was heated to boiling, the stirrer was started and a solution of 1.3649 g. of the above chloro compound in 25 cc. of xylene was added from the separatory funnel during one-half hour. The reaction mixture was heated and stirred for one hour after the addition of the chloro compound was complete. The dark colored reaction mixture was poured on cracked ice, the xylene layer was separated, washed with 50 cc. of 10% sulfuric acid solution and then water. The solution was dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under reduced pressure at ordinary temperatures. The residue was crystallized from alcohol and ether. The yield was 0.3140 g. (26.4% of the theoretical amount) of the hydrocarbon, $C_{38}H_{54}$, m. p. 171–172°. A mixture of this product with a sample of the hydrocarbon prepared by the action of heat on hexa-*tert.*-butylethinylethane[5] melted at 171–172°.

[15] This micro-analysis was made by Mr. K. Eder.

**Reactions of the Hydrocarbon, $C_{38}H_{54}$ Prepared by the Rearrangement of Hexa-*tert.*-butylethinylethane.**—A solution of 0.1 g. of the hydrocarbon in 3 cc. of carbon tetrachloride was treated with a few drops of a 5% solution of bromine in carbon tetrachloride. Only a very small amount of the bromine solution was decolorized.

To a solution of 0.1 g. of the hydrocarbon in 10 cc. of glacial acetic acid was added 3 to 4 drops of tetranitromethane. No color was developed in one hour. At the end of two hours a faint yellow color was noticeable.

Two grams of the hydrocarbon was refluxed with 100 cc. of 5% aqueous potassium permanganate solution for about forty hours. Extraction of this reaction mixture with ether yielded the original substance. After two recrystallizations the recovered product weighed 1.2 g. and melted at 171–172°.

Two grams of the hydrocarbon was dissolved in 30 cc. of dry ether and this solution was shaken with 5 cc. of 40% sodium amalgam in an atmosphere of nitrogen for about twenty-four hours. The solution became deep red in color in about fifteen minutes and was dark brown at the end of the treatment. The amalgam was frozen and the ether solution was decanted off and treated with dry carbon dioxide. The solution was not decolorized and no acid was obtained from the reaction mixture when it was worked up in the usual fashion.

**Attempted Catalytic Reduction of Hexa-*tert.*-butylethinylethane.**—Two grams of hexa-*tert.*-butylethinylethane was dissolved in 100 cc. of absolute alcohol and after the addition of 0.1 g. of platinum-oxide platinum black catalyst,[8] was treated with hydrogen under pressure in a Burgess–Parr reduction apparatus at 70–80°. Apparently no hydrogen was taken up by the solution. On working up the reaction mixture the isomeric hydrocarbon, $C_{38}H_{54}$, was obtained. This was undoubtedly produced by the rearrangement of the true ethane at the elevated temperature.

**Action of Titanium Trichloride on Other Acetylenic Carbinols.**—The action of titanium trichloride on tri-(3-methyl-3-ethylpentinyl-1)-carbinol, *tert.*-butyldi-*tert.*-butylethinylcarbinol, triphenylethinylcarbinol, tri-*iso*propylethinylcarbinol, tricyclohexylethinylcarbinol and ω-*tert.*-butylpropinyldiphenylcarbinol did not yield products which could be separated and characterized.

## Summary

1. Some new acetylenic carbinols have been synthesized and characterized.

2. The reaction of titanium trichloride with three acetylenic carbinols has been studied and found to produce hydrocarbons which are not the expected hexa-substituted ethanes. Two diaryl-monoacetylenic carbinols gave di-indene derivatives. Tri-*tert.*-butylethinylcarbinol gave a dichloro compound which could be converted to an isomer of hexa-*tert.*-butylethinylethane.

3. Some reactions of this isomer of hexa-*tert.*-butylethinylethane have been described.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

# CONDENSATION OF VANILLIN SUBSTITUTION PRODUCTS WITH ACETOPHENONE

BY L. CHAS. RAIFORD AND GLEN V. GUNDY

RECEIVED OCTOBER 23, 1931 PUBLISHED MARCH 5, 1932

Claisen and collaborators[1] showed that acids, caustic alkalies and sodium alcoholate may be used to condense benzaldehyde with acetone to give mono- and dibenzal derivatives. Kostanecki and Rossbach[2] found that with sodium hydroxide as condensing agent benzaldehyde interacts with acetophenone to give benzalacetophenone, benzaldi- and triacetophenones. Yields are not given.

The condensation of vanillin and acetophenone by means of 50% caustic alkali solution at room temperature was studied by Nomura and Nozawa,[3] who obtained a mono- and a diacetophenone derivative. Pearson[4] repeated this work with a "rather more dilute caustic soda" and reported only a monoacetophenone derivative when the experiment was done in winter and the reaction mixture was allowed to stand for seven days; in summer the condensation was complete at the end of three days, and both mono- and diacetophenone derivatives were obtained. In view of these results it was of interest to test the effects of substituents in the starting aldehyde on this condensation.

During the last few years all chlorine and bromine substitution products of vanillin required by theory have been prepared in this Laboratory and condensed with typical amino compounds.[5] Interference with the reaction was noted only in those cases where both positions adjacent to the aldehyde group were substituted, and even then the hindrance was much less than expected. In the benzoin condensation, however, recent work[6] indicates that substituents in positions ortho to the aldehyde radical hinder the reaction. On this account it was desired to condense the halogenated vanillins with acetophenone under the conditions indicated by Schmidt[7] and elaborated by Claisen. It was also of interest to test Pearson's conclusions regarding the kinds and amounts of products formed in terms of variation of time and temperature, and to try to devise a

[1] Claisen and others, *Ber.*, **14**, 349, 2463 (1881); **20**, 657 (1887); *Ann.*, **223**, 137 (1884).

[2] Kostanecki and Rossbach, *Ber.*, **29**, 1488, 2245 (1896).

[3] Nomura and Nozawa, *Rep. Tohôku Univ.*, **7**, 79 (1918).

[4] Pearson, *Pharm. J.*, **103**, 79 (1919).

[5] Raiford and Lichty, THIS JOURNAL, **52**, 4576 (1930). Other important references are given in that report.

[6] Raiford and Talbot, *ibid.*, **54**, 1092 (1932).

[7] Schmidt, *Ber.*, **14**, 1459 (1881).

more suitable method of preparation for these products. It may be stated at once that repetition of Pearson's experiments[8] in summer and in winter gave both mono- and diacetophenone derivatives.[9] Much time was saved and equally good results were obtained by refluxing the reaction mixtures for one and one-half hours instead of allowing them to stand for longer periods at room temperature.

## Experimental Part

The vanillin substitution products were prepared in accordance with the methods already published from this Laboratory. Unless otherwise indicated in the tabular summaries the condensations were carried out as follows. Ten grams each of the substituted vanillin and acetophenone were dissolved in 75 cc. of alcohol, 20 cc. of a 25% solution of sodium hydroxide added, the mixture refluxed for about ninety minutes, cooled, and acidified with hydrochloric acid. This precipitated a mixture of the mono- and diacetophenone derivatives. When this mixture was dissolved in alcohol and the solution allowed to cool, nearly all of the monoacetophenone derivative separated out. The filtrate was heated, diluted, and again cooled to precipitate the diacetophenone compound. The methods of purification and the analytical data are given in the accompanying tables.

TABLE I

VANILLALACETOPHENONE DERIVATIVES

| Substituted vanillal | Yield, % | M. p., °C. | Formula | Analyses Halogen, % Calcd. | Found. |
|---|---|---|---|---|---|
| 2-Bromo- | 18[a] | 114–115[b] | $C_{16}H_{13}O_3Br$ | 24.02 | 24.02 |
| 5-Bromo- | 33 | 124–125[c] | $C_{16}H_{13}O_3Br$ | 24.02 | 24.22 |
| 6-Bromo- | 52[d] | 172–173 | $C_{16}H_{13}O_3Br$ | 24.02 | 24.09 |
| 2,5-Dibromo- | 15 | 145–146[e] | $C_{16}H_{12}O_3Br_2$ | 38.83 | 38.21 |
| 2,6-Dibromo- | 10 | 159[f] | $C_{16}H_{12}O_3Br_2$ | 38.83 | 38.50 |
| 5,6-Dibromo- | 20 | 158.5–160[g] | $C_{16}H_{12}O_3Br_2$ | 38.83 | 38.57 |
| 2,5,6-Tribromo- | 47 | 174[h] | $C_{16}H_{11}O_3Br_3$ | 48.83 | 48.74 |
| 5-Chloro- | 10 | 128[i] | $C_{16}H_{13}O_3Cl$ | 12.30 | 12.27 |
| 6-Chloro- | 10 | 165[j] | $C_{16}H_{13}O_3Cl$ | 12.30 | 12.32 |

[a] Since a mixture of the mono- and diacetophenone derivatives was usually obtained, and separation required many crystallizations, the yields of the purified products only are given. [b] Crystallization from dilute alcohol gave yellow granules. [c] Yellow

[8] The sparing solubility of 5,6-dibromovanillin in alkali solution seemed to prevent condensation with this derivative. The desired results were obtained by refluxing a glacial acetic acid solution of the reactants with concentrated hydrochloric acid for seven hours according to the general method of Glaser and Tramer [*J. prakt. Chem.*, **116**, 332 (1927)].

[9] Regardless of the relative amounts of aldehyde and ketone employed, a mixture of products was obtained where unsubstituted acetophenone was used. Work now in progress, which will be reported later, suggests that only the monoacetophenone derivatives will be obtained when substituted acetophenones are used as starting material.

granules from slightly diluted alcohol. [d] This product was separated from the diacetophenone described below and formed in the same reaction mixture, as follows: crystallization of the entire mass from slightly diluted alcohol gave a mixture of large yellow crystals and small colorless ones, which was well dried and placed in a "trough" made by creasing a large piece of filter paper. The small crystals adhered to the paper more strongly than the larger ones, which were readily removed by lowering one end of the trough and shaking it gently. This yellow material was subjected to five repetitions of this treatment, and then crystallized five times from alcohol. It separated in prisms. [e] Four crystallizations from dilute alcohol gave nearly colorless needles. [f] Purification required fourteen crystallization from dilute alcohol to give fine yellow needles. [g] Four crystallizations from acetic acid followed by two from dilute alcohol gave yellow needles. [h] Colorless granules after two crystallizations from alcohol. [i] Recrystallization four times from alcohol gave yellow granules. [j] Repeated recrystallization of the reaction product gave yellow prisms.

TABLE II

VANILLALDIACETOPHENONE DERIVATIVES

| Substituted vanillal | Yield, % | M. p., °C. | Formula | Analyses Halogen, % Calcd. | Found |
|---|---|---|---|---|---|
| 2-Bromo- | 11[a] | 154–155[b] | $C_{24}H_{21}O_4Br$ | 17.66 | 17.92 |
| 5-Bromo- | 17 | 150–151[c] | $C_{24}H_{21}O_4Br$ | 17.66 | 17.81 |
| 6-Bromo- | 26 | 137[d] | $C_{24}H_{21}O_4Br$ | 17.66 | 17.64 |
| 2,5-Dibromo- | 7 | 134–135[e] | $C_{24}H_{20}O_4Br_2$ | 30.07 | 30.22 |
| 2,6-Dibromo- | 7 | 135[f] | $C_{24}H_{20}O_4Br_2$ | 30.07 | 30.23 |
| 5,6-Dibromo- | 5 | 163–164[g] | $C_{24}H_{20}O_4Br_2$ | 30.07 | 29.90 |
| 2,5,6-Tribromo- | 6 | 163[h] | $C_{24}H_{19}O_4Br_3$ | 39.28 | 39.22 |
| 5-Chloro- | 7 | 151[i] | $C_{24}H_{21}O_4Cl$ | 8.69 | 8.64 |
| 6-Chloro- | 3 | 151[j] | $C_{24}H_{21}O_4Cl$ | 8.69 | 8.57 |

[a] All yields refer to the purified products. [b] Repeated crystallization from alcohol gave small nearly colorless plates. [c] Colorless needles after several crystallizations from dilute alcohol. [d] Fine colorless needles by repeated crystallization from alcohol. [e] Several crystallizations from dilute alcohol gave nearly colorless fine needles. [f] Repeated crystallization from alcohol gave nearly colorless small plates. [g] Very fine colorless needles from acetic acid. [h] Three crystallizations from glacial acetic acid gave very fine colorless needles. [i] Colorless needles after many crystallizations from dilute alcohol. [j] Several recrystallizations from dilute alcohol gave fine colorless needles.

## Summary

1. The bromine and chlorine substitution products of vanillin condense with acetophenone in the presence of sodium hydroxide to give mono- and diacetophenone derivatives.

2. Of the vanillalacetophenones, the three monobromo, the 2,6- and the 5,6-dibromo compounds are yellow; while the 2,5-dibromo and the 2,5,6-tribromo products are practically colorless. The chlorine compounds studied show similar differences. None of the diacetophenone derivatives are colored.

3. Further work is in progress.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF VERMONT]

# DERIVATIVES OF SECONDARY BUTYLBENZENE[1]

BY R. R. READ, C. A. HEWITT AND N. R. PIKE

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During a study of some relationships of the germicidal activity of certain phenols[2] it became necessary to prepare a number of derivatives of secondary butylbenzene. It has seemed desirable to report this work separately.

## Experimental

Normal butyl alcohol was dehydrated by heated aluminum oxide in the furnace described previously[3] and the butylene condensed and dissolved in kerosene. This was extracted twice in the cold with 50% sulfuric acid to remove the isobutylene that might have been formed. No attempt was made to prove the presence of this isomer.

The butylene was distilled out of the kerosene through a cooled refluxing column, dried by passing through a calcium chloride column, and converted into secondary butylbenzene by the usual procedure; 1818 g. of butylene yielded 2150 g. of *sec.*-butylbenzene, b. p. 172–175°.

This was nitrated as in the case of *n*-butylbenzene and fractionated through a packed (glass tubes 5 × 10 mm.) refluxing column one meter long.

*o*-**Nitro-*sec.*-butylbenzene,** b. p. 123–126° (12 mm.), $d_4^{20}$ 1.065. *Anal.* Calcd.: N, 7.8. Found: N, 8.2.

*p*-**Nitro-*sec.*-butylbenzene,** b. p. 142–144° (12 mm.), $d_4^{20}$ 1.065. *Anal.* Calcd.: N, 7.8. Found: N, 8.2.

The nitro derivatives were reduced by tin and hydrochloric acid and by iron and hydrochloric acid.

*o*-**Amino-*sec.*-butylbenzene,** b. p. 120–122° (16 mm.), $d_4^{20}$ 0.957. *Anal.* Calcd.: N, 9.4. Found: N, 9.2.

*p*-**Amino-*sec.*-butylbenzene,** b. p. 130–133° (26 mm.).[4]

The benzoate melted at 130° as reported previously.[4]

The corresponding phenols were prepared from the amines by the usual procedure, the previously described para derivative melting at 61–62°; previous value 59–60°.

*o*-*Sec.*-**butylphenol,** b. p. 116° (21 mm.), 227–228° (corr.). *Anal.* Calcd.: C, 80.0; H, 9.3. Found: C, 79.6; H, 9.2.

These two phenols were later prepared by condensing *sec.*-butyl alcohol with phenol in the presence of zinc chloride. The phenol mixture so obtained was freed from non-phenolic material by extraction of the alkali solution with ligroin. Repeated fractionation through a 90-cm. packed column heated to about 200° produced the separation of the two isomers: *o-sec.*-butylphenol, 227–228°, and *p-sec.*-butylphenol, 240–242°, m. p. 61–62°. A later report will give the details of the condensation of the secondary and tertiary alcohols with phenols.

The *p-sec.*-butylaniline was acetylated with glacial acetic acid and the anilide air dried. This was nitrated[5] at 12°, and the product hydrolyzed. The crude nitro-

[1] Read and Mullin, THIS JOURNAL, **50,** 1763 (1928).

[2] A report of a portion of this is included in a paper by Rettger, Plastridge and Valley, *Centr. Bakt., Parasitenk.*, 287 (1929).

[3] Read and Prisley, THIS JOURNAL, **46,** 1512 (1924).

[4] Reilly and Hickenbotton, *J. Chem. Soc.*, **117,** 103 (1920).

[5] Noyes "Organic Chemistry," H. Holt and Company, New York, 1903.

aniline was converted into the *m*-nitro-*sec.*-butylbenzene in the usual manner by diazotization in alcohol:[6] *m*-nitro-*sec.*-butylbenzene; b. p. 132–134° (19 mm.). *Anal.* Calcd.: N, 7.8. Found: N, 8.0. This was reduced to the amine with tin and hydrochloric acid: *m-sec.*-butylaniline, b. p. 120° (18 mm.). *Anal.* Calcd.: N, 9.4. Found: N, 8.8.

[6] Bigelow, THIS JOURNAL, **41**, 1559 (1919).

BURLINGTON, VERMONT

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[CONTRIBUTION FROM THE LABORATORIES OF SHARP AND DOHME, INC.]

# SOME SUBSTITUTED PHENOLS AND GERMICIDAL ACTIVITY

BY R. R. READ AND ELLIS MILLER

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An increasing interest in the germicidal activity of substituted phenols led the writers to undertake a study of the relation between this property and the nature of certain substituted groups as well as their positions on the ring.

Since it was found, in the case of the alkylresorcinols[1,2,3] that the weight of the hydrocarbon side chain determined the degree of germicidal activity, it seemed desirable to study the influence of weight alone by comparing the effects of differing groups of approximately the same molecular weight. For this purpose a series of substituted phenols, containing oxygen in the side chain, was prepared and compared with normal, secondary and tertiary butylphenols. The activity of a number of other phenols is also included for comparative purposes.

Also in order to study the influence of position in the ring, the ortho, meta and para isomers were prepared in several instances. These compounds and their phenol coefficients are listed in the accompanying table.

## Experimental

The preparation of the three normal butylphenols[4] and of the ortho and para secondary butylphenols from secondary butylbenzene[5] has been reported previously.

The various ethers were all prepared by the usual procedure. One mole of sodium was dissolved in about 15 moles of absolute alcohol and one mole of the phenol added to the solution. The solution was refluxed on a steam-bath while one mole of the alkyl chloride or chlorohydrin was added during one hour. Heating was continued during two hours. The precipitated salt was filtered off and the alcohol removed under reduced pressure. The

[1] Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).

[2] Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926).

[3] See also the work of Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930), which appeared since the work here described was completed.

[4] Read and Mullin, THIS JOURNAL, **50**, 1763 (1928).

[5] Read, Hewitt and Pike, *ibid.*, **54**, 1194 (1932).

TABLE I

STRUCTURAL, PREPARATIONAL, PHYSICAL AND ANALYTICAL DATA

| Side chain on phenol | Position | Weight of side chain | Phenol coefficient[a] | Melting point, °C. | Crystallizing solvent[b] | Analyses, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|---|---|---|
| $CH_2CH_2CH_2CH_3$ | *o* | 57 | 52 (a) | B. p. 234–237 | | | | | |
| | *m* | 57 | 52 (a) | B. p. 247–249 | | | | | |
| | *p* | 57 | 52 (a) | B. p. 246–250[c] | | | | | |
| $CH(CH_3)CH_2CH_3$ | *o* | 57 | 28.1 (a) | B. p. 226–228 | | 80.0 | 9.3 | 79.6 | 9.2 |
| | *p* | 57 | 27.5 (a) | B. p. 240–242 | e | | | | |
| | | | | 61–62 | | | | | |
| $C(CH_3)_3$ | *p* | 57 | 19 (b) 22 (c) | 99 | e | | | | |
| $OCH_2CH_2OH$ | *o* | 61 | 0 (b) | 96–97 | h i | 62.3 | 6.5 | 62.1 | 6.7 |
| | *m* | 61 | 0 (b) | 83–85 | h | 62.3 | 6.5 | 62.9 | 6.8 |
| | *p* | 61 | 0 (b) | B. p. 202–205 (14 mm.) | | 62.3 | 6.5 | 62.5 | 6.5 |
| $OCH_2CHOHCH_2OH$ | *o* | 91 | 0 (b) | B. p. 245–255 (18 mm.) | | 58.7 | 6.5 | 58.5 | 6.5 |
| $OCH_2CH_2CH_3$ | *o* | 59 | 5.5 (b)[d] | B. p. 228–229 (corr.) | | | | | |
| | *p* | 59 | 4.4 (b) | 55 | e f g | 71.1 | 7.9 | 70.9 | 7.9 |
| $OCOCH_3$ | *o* | 59 | 0 (b) | B. p. 148 (25 mm.) | | | | | |
| | *m* | 59 | 0 (b) | B. p. 174 (24 mm.) | | | | | |
| | *p* | 59 | 0 (b) | B. p. 167–170 (20 mm.) | | | | | |
| | | | | 53–54 | | | | | |
| $COOCH_3$ | *o* | 59 | 0 (b) | B. p. 109–111 (16 mm.) | | | | | |
| $COOCH_3$ | *p* | 59 | 0 (b) | 123–124 | | | | | |
| Cyclohexyl | *p* | 83 | 0 (b)[e] | 126 | e | | | | |
| Cyclohexyl | *o* | .. | 32 (b) | 52 | e | | | | |
| $OCH_2CH_2CH_2CH_2CH_2CH_3$ | *p* | 101 | 67 (c) | 44 | e | | | | |
| $OCH_2CH_2CH_2CH_2CH_3$ | *p* | 87 | 40 (c) | 48 | e | | | | |
| $C_6H_3(OH)_2(OCH_2CH_2OH)$ | | | 0 (b) | B. p. 195–205 (13 mm.) | | 56.4 | 5.9 | 56.7 | 5.8 |
| $CH_2OH$ | *o* | 31 | 0 (b) | 85 | | | | | |
| $OCH_3$ | *o* | 31 | 0.8 (c) | 26–28 | | | | | |
| | *m* | 31 | 0.7 (c) | B. p. 140–142 (15 mm.) | | | | | |
| | *p* | 31 | 0.8 (c) | 47–48 | | | | | |
| $C_2H_5$ | *p* | 29 | 7[f] | | | | | | |
| $CH_3$ | *o* | 15 | 2.2 (a) | 29 | | | | | |
| | *m* | 15 | 2.2 (a) | 6 | | | | | |
| | *p* | 15 | 2.2 (a) | 33 | | | | | |

[a] Phenol coefficients by the Hygienic Laboratory Method, 20°; organism, *Staph. aureus;* (a), (b), (c), refer to the bacteriologist making determinations.

[b] Crystallizing solvents: e, ligroin; f, water; g, ethyl alcohol; h, benzene; i, carbon tetrachloride.

[c] Due to a typographical error, this value was stated to be 746–750° by Read and Mullin, THIS JOURNAL, **50,** 1764 (1928).

[d] Klarmann, THIS JOURNAL, **53,** 3402 (1931), gives a value of 5.4 for the meta isomer using the same test organism, *Staph. aureus.*

[e] Bartlett and Garland, *ibid.*, **49,** 2100 (1927), also found *p*-cyclohexylphenol inactive. Solubility at 25° is 6:100,000. The ortho isomer is active at 1:3200.

[f] Schaffer and Tilley, Ref. 7,

phenol then was distilled in vacuum and crystallized from the solvent indicated. Analyses are given if the compounds have not been described previously.

Tertiary butylphenol, tertiary amylphenol and cyclohexylphenols were prepared by the condensation of the corresponding alcohols with phenol in the presence of zinc chloride, as will be described in a later report. Ortho and para secondary butylphenols can also be obtained by the condensation of secondary or primary butyl alcohol with phenol but the separation of the isomers is difficult.

## Discussion

As the three cresols gave practically identical values,[6,7,8] it was hoped that if the bactericidal activity were sufficiently enhanced, a variation would appear. The normal butylphenols[9] did not show such a variation, having an average value of fifty for each isomer on one series of determinations and a value of fifty-two on a second series.[10]

It appears then that in the case of certain alkyl phenols (monohydroxybenzene derivatives) the relative position on the ring of the alkyl and

[6] An average of six determinations gave values 2.16, 2.17 and 2.20 for the *o*, *m* and *p* isomers. These values are taken from determinations reported by Leo F. Rettger.

[7] Schaffer and Tilley, *J. Bact.*, **14,** 266 (1927), give the values 2.2 for ortho cresol and 2.4 for meta cresol. The somewhat higher values reported by these investigators are probably due to the use of a higher temperature, 25°. It is interesting that their values for thymol and carvacrol, which differ only in the position of the OH group, are so nearly identical, 28.5 and 27.5.

[8] It has been the writers' experience that determinations of the phenol coefficient of a single lot of a phenol by the same bacteriologist made on different occasions may vary over a range of 10%. This is particularly true when the coefficient is high. The variation between different workers may be even greater. A very extreme case was noted when a sample was divided among three well-known bacteriologists who reported values from twenty-two to forty.

[9] The normal butylphenols were prepared for Rettger, Plastridge and Calley [*Centr. Bakt. Parasitenk.*, 287 (1929)], who investigated the properties of the butylphenols which one of the writers (R.) prepared for them.

[10] Schaffer and Tilley, *J. Bact.*, **12,** 307 (1926), assign a value of sixty-eight to the *p-n*-butylphenol. These workers used a temperature of 25° instead of the 20° used in the work reported here. B. Hampil, *J. Infectious Diseases,* **43,** 9 (1928), discusses some effects of temperature variation. Coulthard, Marshall and Pyman have recently assigned the values of 70 for the para and 75 for the ortho isomer using *B. typhosus* as the test organism.

hydroxyl groups has little effect on the germicidal activity: all three isomers are of approximately equal activity.

In the case of certain sulfur-containing phenols, a dependence is evident. The three hydroxydiphenyl sulfides[11] offer a striking variation in activity, having coefficients of 33, 68 and 115 for the *o*, *m* and *p* isomers. A later report on certain sulfur-containing germicides by the authors will show a similar variation in activity between isomers.

It has been observed previously that the mass of the side chain attached to the phenolic nucleus is only one factor in determining the activity of a phenol as a germicide. Particularly has it been pointed out that branching of the side chain lowers the activity in the resorcinol series.[2,12] This effect of a branching alkyl chain is demonstrated more clearly in the series of butylphenols, in which the values decrease in the order normal, secondary, tertiary in a ratio 5:3:2.

Frequently phenols which should be very active as tested by the usual[13] procedure are inactive due to low solubility. The two cyclohexylphenols offer an odd illustration of what is apparently such a case: the ortho isomer is active[14] while the para is not.[15] The para isomer is soluble to the extent of 6 mg. in 100 cc. of water while the coefficient of thirty would require a solubility of approximately 48 mg. per 100 cc. The still less soluble *p*-*n*-hexylphenol is also inactive according to this method of testing, although in the presence of alkali this phenol is reported to have a coefficient of 90.[16] Secondary hexylphenol (a mixture of the *o* and *p* isomers) is likewise inactive at 20° but at 37° and in the presence of 0.2% sodium carbonate is markedly active.[17] Coulthard, Marshall and Pyman[16] and also Hampil[18] found it necessary to use a dilute solution of alkali as the solvent in order to make comparisons of many alkyl cresols, resorcinols and guaiacols. This procedure probably alters the activity of the phenol as is indicated by tertiary butylphenol and its sodium salt.[19]

The replacement of a methylene group by oxygen lowers the activity of the substituted phenol markedly: *p*-*n*-butylphenol 50, and *p*-hydroxyphenyl *n*-propyl ether 5; *p*-ethylphenol 7, and *p*-methoxyphenol 1. When, in addition, the terminal methyl group of such an ether or one of the hydrogen atoms of that group is replaced by an hydroxyl group, the germicidal

[11] Johnson and Hilbert, THIS JOURNAL, **51**, 1534 (1929).

[12] Leonard, *A. M. A.*, **83**, 2005 (1924); *J. Urology*, **585**, 12 (1924).

[13] Hygienic Laboratory Method.

[14] Coefficient 32.

[15] Bartlett and Garland also report the para isomer as inactive, THIS JOURNAL, **49**, 2098 (1927).

[16] Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).

[17] Coefficient 78, less than *p*-*n*-hexylphenol as would be expected.

[18] Hampil, *J. Infectious Diseases*, **43**, 25 (1928).

[19] *p*-Tertiary butylphenol 19, sodium salt 13.

activity goes down to less than one—less than if no side chain were present: *p*-hydroxylphenyl *n*-propyl ether 5, *p*-hydroxyphenyl *n*-γ-hydroxypropyl ether 0; *o*-cresol 2.2, saligenin 0.

## Summary

While it is true that no concise "rules" can result from such limited data, certain conclusions are perhaps permissible.

1. The mass of a group substituted into a phenol has little relation to the germicidal activity of the resulting compound.
2. Position isomerism has little effect on the bactericidal activity of alkyl and alkoxy substituted phenols.
3. Side chain isomerism affects the activity of alkyl phenols markedly. The more compact the group, the lower the activity.
4. The group $CH_2R$ is much more effective than OR in enhancing the activity of a phenol.
5. The carbomethoxy and acetoxy groups are ineffective in enhancing the activity of phenol.

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

# THE NITRATION OF PHENYLACETIC ACID

BY DAVID L. YABROFF AND C. W. PORTER

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Latimer and Porter have shown that the directive influence of a group substituted for hydrogen in the benzene ring depends upon the residual charge of the atom attached to the ring.[1] The method of determining the residual charge is based upon the unequal sharing of electrons between two unlike atoms. It was found that if the residual charge on the atom attached to the ring has a high positive value, the substituent directs the incoming group mainly to the meta position and if the residual charge is zero or negative the substituent is ortho–para in its orienting influence. The method used in calculating the residual charge does not take into account the influence of atoms beyond those directly connected with the key atom. In order to evaluate the influences of remote atoms it is necessary to have exact data on the behavior of border-line groups. As a start in this direction we have studied the nitration of phenylacetic acid.

Radziszewski[2] found that the nitration of phenylacetic acid yielded mostly the para isomer, which is quite insoluble, and a small amount of the ortho isomer, which remained behind in the mother liquor. Maxwell,[3]

[1] Latimer and Porter, THIS JOURNAL, **52**, 206 (1930).

[2] Radziszewski, *Ber.*, **2**, 207 (1869); **3**, 648 (1870).

[3] Maxwell, *ibid.*, **12**, 1764 (1879).

Bedson[4] and later Borsche[5] also studied the nitration of phenylacetic acid, but in no case is any mention made of the formation of the meta derivative. The nitration of the ethyl ester of phenylacetic acid was carried out qualitatively by Radziszewski[2] and quantitatively by Baker and Ingold[6] and by Flürscheim and Holmes.[7] Baker and Ingold found that approximately 9% of the meta derivative was formed whereas Flürscheim and Holmes obtained about 12% of the meta derivative. Baker and Ingold state that undissociated phenylacetic acid should yield an even higher proportion of the meta derivative, but the effect of ionization might be a large contrary factor. The negative charge induced by ionization would tend to make the effective residual charge on the key atom more negative, and hence more ortho–para in its orienting power. The similar case of the benzoate ion has been discussed by Flürscheim and Holmes.[8] From the results of Holleman[9] and Zaki,[10] who found that benzoic acid yields more of the meta compound than do its esters, we should expect phenylacetic acid to yield a higher proportion of the meta isomer than would be obtained from its esters. Actually we obtained 14.4% of the meta derivative upon the nitration of phenylacetic acid.

**Analytical Method.**—The nitro bodies obtained from phenylacetic acid by nitration were oxidized with alkaline permanganate to the corresponding nitrobenzoic acids. The total quantity of nitrobenzoic acid (ortho, meta and para) obtained in this way was determined by titration with titanium trichloride. The nitrobenzoic acids were converted into aminobenzoic acids by reduction and the amino acids were treated with bromine water. By this process the ortho and para aminobenzoic acids were converted into tribromoaniline which precipitated and the meta compound was converted into 2,4 6-tribromo-3-aminobenzoic acid, which remained in solution. The tribromoaniline was filtered off and weighed to obtain the quantity of the ortho and para nitrobenzoic acids present. The meta isomer was determined by the difference between the total quantity of nitrobenzoic acids formed and the quantity of mixed ortho and para nitrobenzoic acids. This procedure is a modification of the method used by Flürscheim and Holmes[11] for the analysis of a mixture of aminobenzoic acids.

Each step of our entire process was checked by isolating the products at all the intermediate stages and by repeating each step with known syn-

[4] Bedson, *J. Chem. Soc.*, **37**, 90 (1880).
[5] Borsche, *Ber.*, **42**, 3596 (1909–1910).
[6] Baker and Ingold, *J. Chem. Soc.*, 832 (1927).
[7] Flürscheim and Holmes, *ibid.*, 1607 (1928).
[8] Flürscheim and Holmes, *ibid.*, **128**, 1565 (1926).
[9] Holleman, *Rev. trav. Chim.*, **18**, 267 (1899).
[10] Zaki, *J. Chem. Soc.*, 983 (1928).
[11] Flürscheim and Holmes, *ibid.*, 448 (1928).

thetic mixtures. Finally, artificial mixtures consisting of the three nitrophenylacetic acids, phenylacetic acid and nitric acid were put through the procedure and the percentage of the meta derivative found was well within 1% of that calculated.

## Experimental Section

**Reagents.**—*Meta*-nitrophenylacetic acid was prepared from *m*-nitrotoluene. The nitrotoluene (68 g. or 0.5 mole) was kept at 135–145° while 84 g. of bromine (5% excess) was slowly added from a dropping funnel (compare Wachendorff)[12] while the mixture was mechanically stirred. Reaction occurred readily as shown by a steady bubbling of the mixture with a constant evolution of hydrogen bromide. The addition of the bromine took approximately an hour and the mixture was kept at the above temperature for half an hour longer and then allowed to cool. When the temperature is allowed to rise above 145°, resinous substances are produced and the yield is poor. A saturated solution of 32.5 g. of potassium cyanide (0.5 mole) in water and 300 cc. of alcohol was then added to the impure nitrobenzyl bromide and the reaction mixture was refluxed for three hours on a water-bath. The alcohol was distilled off and the nitrobenzyl cyanide was hydrolyzed by refluxing with 350 cc. of concentrated hydrochloric acid for three hours (see Gabriel and Borgmann).[13] The hydrolyzed mixture was filtered through glass wool while still hot and then allowed to cool. The cooled solution deposited crystals of *m*-nitrophenylacetic acid after a few hours. A second crop of crystals was obtained by evaporating the mother liquor to half of its volume. The crude *m*-nitrophenylacetic acid was repeatedly recrystallized from water and dried under reduced pressure over calcium chloride (m. p. 119.5–120°). On the basis of the nitrotoluene used a 62% yield (56 g.) of the purified product was obtained.

Phenylacetic acid, *o*-nitrophenylacetic acid and *p*-nitrophenylacetic acid were available on the market. The commercial products were purified by fractional crystallization. Kahlbaum's nitric acid was freed from oxides of nitrogen by bubbling dry air through it under reduced pressure for three to four hours. At the end of this time the resulting liquid had only a very pale yellow color.

## Procedure

**Nitration.**—Dried and finely pulverized phenylacetic acid (approximately 5 g.) was added in small portions to 30 cc. of nitric acid free from oxides of nitrogen and having a density of 1.495. The temperature was kept at 0° and the flask was shaken thoroughly after each small addition of the phenylacetic acid. The mixtures were then allowed to stand for three hours at 0°. At the end of this time the mixture was poured onto cracked ice and the precipitated nitro bodies were filtered off. The precipitate was freed from nitric acid by washing with water until the wash water no longer gave a test with diphenylamine and sulfuric acid.[9] The washings and filtrate were combined and extracted with ether and the ether extracts were washed with water. All of the ether extracts were combined, dried over anhydrous sodium sulfate and the solvent was distilled off. The nitro bodies obtained from the filtrate and from the precipitate were then combined and subjected to analysis. Equivalent weight determinations showed that neither dinitration nor oxidation occurred with nitric acid of density 1.495 when the reaction mixture was kept at 0°.

**Oxidation of Nitrophenylacetic Acids.**—The oxidation of the $-CH_2COOH$ group with alkaline permanganate goes in steps[14] through $-CHOHCOO^-$, $-COCOO^-$ and

[12] Wachendorff, *Ann.*, **185**, 277 (1887).

[13] Gabriel and Borgmann, *Ber.*, **16**, 2064 (1883).

[14] Prjevalsky, *J. Russ. Phys.-Chem. Soc.*, **49**, 567 (1917–1918).

finally to $-COO^-$ and $CO_3^{--}$. To be of value the oxidation in this case must proceed to the last step without changing the ratio between the isomers present. Synthetic mixtures composed of the ortho, meta and para-nitrophenylacetic acids were oxidized under varying conditions. The equivalent weights of the oxidation products, the percentage recovery and the percentage of the *m*-derivative present in each mixture were determined.

The oxidation conditions were varied as follows: (1) time of reaction, 4, 8, 10 and 12 hours; (2) excess of permanganate, 10, 20, 30 and 50%; (3) hydroxide-ion concentration, 0.01, 0.1, 0.25 and 0.50 normal. The following procedure was finally adopted. The theoretical amount of solid permanganate was added all at once, the volume of the solution being adjusted so that a 2% permanganate solution resulted. The hydroxide-ion concentration was kept at 0.1 normal. The temperature was maintained at 95–100°. Samples were withdrawn from the oxidation vessels every hour, and the manganese dioxide was allowed to settle. If the clear liquid above the manganese dioxide was not violet, additional permanganate was added and the mixture was heated again. The process was continued until permanganate was still present after two hours of continuous heating. Usually the reactions were over in four to six hours. Under these conditions the recovery of the oxidation products was about 90% of the theoretical and with artificial mixtures of known composition the percentage of the meta compound found was within 1% of the actual value.

After the oxidation had been completed, the manganese dioxide was filtered off and extracted with three 250 cc. portions of boiling water. The aqueous extracts and the original filtrate were combined and evaporated to about 500 cc. The clear solution was then acidified with sulfuric acid and the precipitated nitrobenzoic acids were filtered off. The precipitate was washed with water and the washings and filtrate were combined and extracted with three 150 cc. portions of ether. The ether extracts were combined and dried, and the solvent was distilled off. The residue thus obtained was combined with the originally precipitated acids, the benzoic acid present was sublimed off and equivalent weight determinations were made with titanium trichloride.

**Reduction of the Nitrobenzoic Acids.**—A weighed amount of the mixed nitrobenzoic acids was dissolved in a known volume of standardized sodium hydroxide solution and the resulting alkalinity of the stock solution was then calculated. Samples (50 cc. portions) were pipetted from the stock solution and a sufficient quantity of concentrated hydrochloric acid was added to give a four normal solution for a 300-cc. volume. A measured excess of titanium trichloride was added and the mixture was gently boiled for ten minutes. If the solution became colorless during boiling, a small amount of titanium trichloride was added and the boiling continued until a slight violet color remained after ten minutes' boiling. (For methods of using titanium trichloride see Knecht and Hibbert.[15])

**Bromination of the Aminobenzoic Acids.**—By a series of experiments with known mixtures of ortho, meta and para-aminobenzoic acids we were able to modify the methods of Francis and Hill[16] and of Flurscheim and Holmes[11] so as to obtain a nearly quantitative bromination and we were able to apply a systematic correction for the difference between the theoretical yield and the quantity obtained. The following technique was adopted: (a) a sample of the mixed nitrobenzoic acids (approximately 2.5 g.) was dissolved in 500 cc. of 0.1 *N* sodium hydroxide. (b) A 50 cc. portion of this solution was acidified by the addition of 95 cc. of 12 *N* hydrochloric acid and heated with a measured excess of titanium trichloride. (c) To the clear cooled solution 30 cc. of 95% alcohol

[15] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., New York, 1925.

[16] Francis and Hill, THIS JOURNAL, **46**, 2498 (1924).

was added and the solution was warmed to 40°. (d) Bromine water was added until the solution had a permanent pale yellow color. (e) The mixture was diluted to 300 cc. and the acidity was adjusted to exactly four normal. (f) The precipitate was allowed to stand in contact with the mother liquor for twenty-four hours. (g) The residue was filtered, washed and then dried over calcium chloride in a vacuum desiccator and weighed.

Under these conditions *m*-aminobenzoic acid is brominated in the 2,4,6-positions, yielding tribromo-*m*-aminobenzoic acid, which is soluble in water. The ortho and para-aminobenzoic acids are converted into tribromoaniline, the carboxyl group being replaced by bromine. An addition of 0.036 g. is made to the weight of the precipitate to cover the loss due to the solubility of the product and possibly due in part to incomplete bromination. This correction is the average of many determinations made on equivalent quantities of known mixtures.

**Estimation of the Total Nitrobenzoic Acids.**—Samples of the stock solution (50-cc. portions of the solution described under bromination) were withdrawn, acidified and mixed with a measured excess of standardized titanium trichloride. The mixture was placed in a water-bath at 90° for twenty minutes. A continuous stream of carbon dioxide was passed over the surface of the liquid to avoid oxidation of the reagent by the air. After cooling, the excess of titanium trichloride was back-titrated with a solution of ferric alum, using ammonium thiocyanate as the indicator.

The results for the last group of nitrations are given in Table I, where the figures for the molecular weights, the titrations and the brominations represent averages of three determinations.

TABLE I

RESULTS OF EXPERIMENTS

| Nitration number | 1 | 2 | 3 |
|---|---|---|---|
| Weight nitrated in grams | 5.13 | 5.05 | 5.65 |
| Weight of nitro bodies obtained in grams | 6.68 | 6.67 | 7.45 |
| Percentage nitration yield | 98 | 99 | 99 |
| Molecular weight of nitration product | 181.6 | 182.2 | 181.0 |
| Weight oxidized in grams | 5.54 | 5.47 | 5.54 |
| Weight of oxidation product obtained in grams | 4.55 | 4.58 | 4.70 |
| Percentage oxidation yield | 89 | 91 | 92 |
| Weight of benzoic acid sublimed in grams | 0.031 | 0.009 | 0.042 |
| Percentage of benzoic acid present in product | 0.7 | 0.2 | 0.8 |
| Molecular weight of oxidation products | 166.8 | 166.4 | 166.7 |
| 0.2485 *N* $TiCl_3$, cc. | 28.14 | 29.60 | 29.81 |
| Total nitrobenzoic acids present in grams | 0.1946 | 0.2048 | 0.2062 |
| Grams of tribromoaniline +0.036 | .329 | .345 | .350 |
| *o-p*-Nitrobenzoic acids present in grams | .1666 | .1747 | .1773 |
| Percentage of meta compound | 14.4 | 14.7 | 14.0 |

The molecular weight calculated for a mono-nitrophenylacetic acid is 181.1; that for a mono-nitrobenzoic acid is 167.05.

## Summary

The nitration of phenylacetic acid has been studied quantitatively. A method of analysis developed by Flürscheim and Holmes has been modified to meet the requirements of this investigation. Optimum conditions

have been established for the nitration of phenylacetic acid, the oxidation of nitrophenylacetic acids, the reduction of these compounds to amino acids and the bromination of aminobenzoic acids. Using this procedure, which yields reproducible results, it was found that 14.4% of the meta isomer is formed when nitric acid at 0° acts upon phenylacetic acid.

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[CONTRIBUTION FROM THE PLAUT RESEARCH LABORATORY OF LEHN & FINK, INC.]

# BACTERICIDAL PROPERTIES OF MONOETHERS OF DIHYDRIC PHENOLS. III. THE MONOETHERS OF PYROCATECHOL. COMPARATIVE NOTES ON THE THREE SERIES OF MONOETHERS

BY EMIL KLARMANN, LOUIS W. GATES AND VLADIMIR A. SHTERNOV

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The third and last group of monoethers studied in this series of investigations[1] comprises the derivatives of pyrocatechol.

The antibacterial action of the parent compound pyrocatechol and of its methyl ether, guaiacol has been studied by many investigators in the past. It is not intended to give a complete tabulation of these findings; the general conclusion may be drawn from them, that as a bactericidal agent, pyrocatechol is less effective than phenol while guaiacol shows practically the same potency as phenol. This is not true, however, of the inhibitory action. Thus according to Cooper and Mason[2] the minimum concentration of pyrocatechol required to inhibit the growth of *B. coli* at 37° is almost one-half that of phenol, while in the case of *B. fluorescens liquefaciens* it is even less.

The preparation of certain higher alkyl monoethers of pyrocatechol from the corresponding diethers is referred to in the German patents Nos. 78,910, 92,651 and 94,852.[3] However, the antibacterial efficacy of these ethers does not appear to have been determined. In addition to these compounds the phenyl monoether is also known. It has been prepared by Ullmann and Stein[4] by treating the solution of the methyl phenyl ether of pyrocatechol in benzene with aluminum chloride.

The series of monoethers of pyrocatechol prepared and studied by us comprises the straight chain aliphatic derivatives up to and including the *n*-heptyl ether, the *sec.*-amyl ether, the phenyl ether and the alphyl aromatic derivatives up to and including the phenyl propyl ether.

In preparing these compounds we followed generally the methods applied

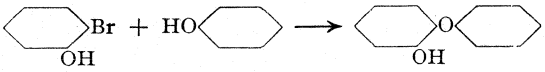
[1] Klarmann, Gatyas and Shternov, THIS JOURNAL, **53**, 3397 (1931); **54**, 298 (1932).

[2] F. A. Cooper and J. Mason, *J. Hygiene*, **26**, 118 (1927).

[3] Friedländer, *Fortschritte der Teerfarbenfabrikation*, **4**, 122–124.

[4] F. Ullmann and A. Stein, *Ber.*, **39**, 623 (1906).

in the preparation of the resorcinol and hydroquinone monoethers, *i. e.*, utilizing the reactivity of the halogen alkyl and alpharyl compounds with the phenolic hydroxyl group. The phenyl ether (*o*-hydroxydiphenyl oxide) which cannot be prepared by this reaction was obtained by condensation of *o*-bromophenol with potassium phenolate in the presence of copper catalyst.




**Bactericidal Action of the Monoethers of Pyrocatechol.**—The bactericidal action of the monoethers of pyrocatechol was determined with *B. typhosus* and *Staph. aureus* as test organisms. The minimum concentrations required to kill the bacteria in five, ten and fifteen minutes at 37°, and the phenol coefficients calculated therefrom, are given in Table I.

TABLE I

BACTERICIDAL ACTION OF MONOETHERS OF PYROCATECHOL

| | *B. typhosus* Bactericidal concentrations | | | Phenol coeff. | *Staph. aureus* Bactericidal concentrations | | | Phenol coeff. |
|---|---|---|---|---|---|---|---|---|
| | 5 min. | 10 min. | 15 min. | | 5 min. | 10 min. | 15 min. | |
| Pyrocatechol | 1:110 | 1:140 | 1:150 | 0.87 | 1:40 | 1:45 | 1:55 | 0.58 |
| **Aliphatic Ethers** | | | | | | | | |
| Methyl | 1:120 | 1:130 | 1:140 | 0.91 | 1:55 | 1:60 | 1:60 | 0.73 |
| Ethyl | 1:225 | 1:275 | 1:275 | 1.8 | 1:120 | 1:120 | 1:130 | 1.6 |
| *n*-Propyl | 1:500 | 1:600 | 1:650 | 4.1 | 1:275 | 1:300 | 1:300 | 3.8 |
| *n*-Butyl | 1:1400 | 1:1500 | 1:1600 | 9.8 | 1:750 | 1:750 | 1:800 | 10 |
| *n*-Amyl | 1:3250 | 1:3250 | 1:3250 | 22 | 1:1800 | 1:1800 | 1:2000 | 23 |
| *Sec.*-amyl | 1:2500 | 1:2750 | 1:2750 | 18 | 1:1400 | 1:1500 | 1:1600 | 20 |
| *n*-Hexyl | 1:2500 | 1:2500 | 1:2500 | 17 | 1:2000 | 1:2250 | 1:2500 | 28 |
| *n*-Heptyl | 1:1200 | 1:1400 | 1:1600 | 9.7 | 1:2500 | 1:2750 | 1:3250 | 37 |
| **Aromatic Ethers** | | | | | | | | |
| Phenyl | 1:2250 | 1:2500 | 1:2500 | 17 | 1:800 | 1:850 | 1:850 | 11 |
| Benzyl | 1:2500 | 1:2750 | 1:2750 | 19 | 1:900 | 1:1200 | 1:1200 | 15 |
| Phenylethyl | 1:3250 | 1:3250 | 1:3500 | 22 | 1:1000 | 1:1600 | 1:1800 | 21 |
| Phenylpropyl | 1:2000 | 1:2000 | 1:2500 | 15 | 1:1300 | 1:1500 | 1:1600 | 19 |
| **Control** | | | | | | | | |
| Phenol (av.) | 1:130 | 1:140 | 1:160 | 1 | 1:70 | 1:80 | 1:90 | 1 |

Thus the bactericidal action of pyrocatechol monoethers appears to be a function of the molecular weight and of the structure of the substituting radical. In the case of the aliphatic ethers the germicidal power against *B. typhosus* increases steadily, reaching a maximum with the *n*-amyl derivative, while with *Staph. aureus* no maximum is observed up to the *n*-heptyl compound. The *sec.*-amyl ether is less effective against either organism than the normal compound. Among the aromatic ethers the phenylethyl derivative is the most effective against both *B. typhosus* and *Staph. aureus*.

**Comparison of the Bactericidal Action of the Monoethers of the Three Dihydric Phenols.**—When comparing the bactericidal potency of the monoethers of the three dihydric phenols (Table II), it is found that the monoethers of pyrocatechol are generally less effective than the corresponding hydroquinone and resorcinol derivatives. Some exceptions are found among the aromatic monoethers, the pyrocatechol phenylpropyl monoether being more effective against *B. typhosus*, and the benzyl ether against *Staph. aureus* than the corresponding hydroquinone ethers. In no case, however, is the germ-killing potency of the resorcinol ethers surpassed by that of the corresponding pyrocatechol compounds.

TABLE II

COMPARISON OF THE BACTERICIDAL ACTION OF THE MONOETHERS OF THE THREE DIHYDRIC PHENOLS

| | Phenol coefficients | | | | | |
|---|---|---|---|---|---|---|
| | *B. typhosus* | | | *Staph. aureus* | | |
| | Resorcinol 0.4 | Hydroquinone >12 | Pyrocatechol 0.87 | Resorcinol 0.4 | Hydroquinone 0.44 | Pyrocatechol 0.58 |
| **Aliphatic Groups** | | | | | | |
| Methyl | 1.3 | 1.0 | 0.91 | 1.2 | **0.8** | **0.73** |
| Ethyl | 3.6 | 1.5 | 1.8 | 3.0 | 1.5 | **1.6** |
| *n*-Propyl | 6.9 | 5.4 | 4.1 | 5.4 | 4.1 | **3.8** |
| *n*-Butyl | 20 | 14 | 9.8 | 18.0 | 9.3 | 10 |
| *n*-Amyl | 38 | 29 | 22 | 36 | 30 | 23 |
| *Sec.*-amyl | 26 | 19 | 18 | 31 | 26 | 20 |
| *n*-Hexyl | 46 | 18 | 17 | 125 | 100 | 28 |
| *n*-Heptyl | 21 | 17 | 9.7 | 330 | 200 | 37 |
| *n*-Octyl | 2.3 | | | 580 | 360 | |
| **Aromatic Groups** | | | | | | |
| Phenyl | 40 | 41 | 17 | 37 | 28 | 11 |
| Benzyl | 21 | 21 | 19 | 16 | 14 | 15 |
| Phenylethyl | 35 | 25 | 22 | 39 | 29 | 21 |
| Phenylpropyl | 34 | 10 | 15 | 89 | 13 | 10 |

This is rather remarkable if one considers that of the three dihydric phenols resorcinol shows the lowest bactericidal potency. Another noteworthy fact is that in the case of the pyrocatechol and hydroquinone monoethers the maximum germicidal action upon *B. typhosus* is shown by the *n*-amyl derivatives, while in the case of resorcinol the potency of the *n*-hexyl ether surpasses that of the *n*-amyl derivative. The bactericidal efficacy of the higher aliphatic ethers of pyrocatechol against *Staph. aureus* is very much below the rather spectacular efficacies of the corresponding resorcinol and hydroquinone monoethers.

The conditions encountered are also evident from Figs. 1 to 3, Figs. 1 and 2 showing the relation between the molecular weight of the substituting aliphatic group and the germicidal effect upon *B. typhosus* and

*Staph. aureus*, respectively, while Fig. 3 deals with the effect of the aromatic ethers upon both bacteria.

The bacteriological experiments are being continued with the following pathogenic germs: *B. coli*, *B. pyocyaneus*, *Streptococcus haemolyticus* and *Vibrio cholerae*. Preliminary results indicate that the Gram negative *B. coli* and *B. pyocyaneus* behave like the Gram negative *B. typhosus* when exposed to the compounds under discussion, while the Gram positive *Strept. haemolyticus* resembles *Staph. aureus* very closely in this respect. *Vibrio cholerae* is enormously sensitive to some of these compounds, but it reacts more like the Gram positive bacteria in spite of its Gram negative character. It is known to behave in this fashion in other instances also.

A detailed description of the bacteriological and toxicological findings will be reported elsewhere.

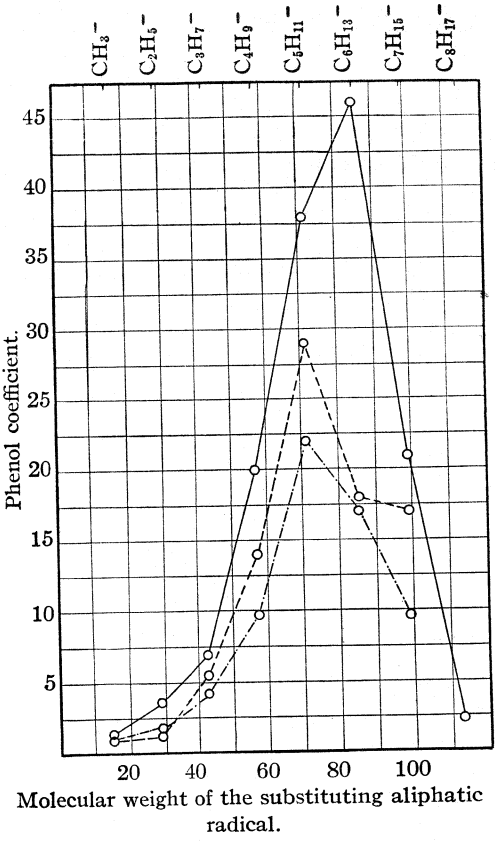
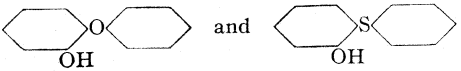



Fig. 1.—The effect of the molecular weight of the aliphatic radical on the bactericidal action of monoethers of dihydric phenols. Test organism, *B. typhosus:* ——, resorcinol monoethers, — — —, hydroquinone monoethers; — · — · —; pyrocatechol monoethers.

The phenyl ethers of the three dihydric phenols, which may also be regarded as isomeric hydroxyphenyl oxides, permit a comparison from the point of view of germicidal potency with the corresponding three isomeric hydroxydiphenyl sulfides prepared by Hilbert and Johnson.[5] This matter already has been referred to in our preceding publication[1] with emphasis upon the differences in the testing methods. The compounds under consideration are, *e. g.*, in the case of the pyrocatechol phenyl ether




[5] G. E. Hilbert and T. B. Johnson, THIS JOURNAL, 51, 1526 (1929).

Thus, *caeteris paribus*, such a comparison is ultimately one of the effect of oxygen and of sulfur, respectively, serving as connecting links of the two nuclei, upon the bactericidal action of the two classes of compounds.

TABLE III

COMPARISON OF THE BACTERICIDAL ACTION UPON *B. Typhosus* OF HYDROXYDIPHENYL OXIDES AND SULFIDES

| | Phenol coeff. | | Phenol coeff. |
|---|---|---|---|
| *o*-Hydroxydiphenyl oxide | 17 | *o*-Hydroxydiphenyl sulfide | 33 |
| *m*-Hydroxydiphenyl oxide | 40 | *m*-Hydroxydiphenyl sulfide | 68 |
| *p*-Hydroxydiphenyl oxide | 41 | *p*-Hydroxydiphenyl sulfide | 115 |

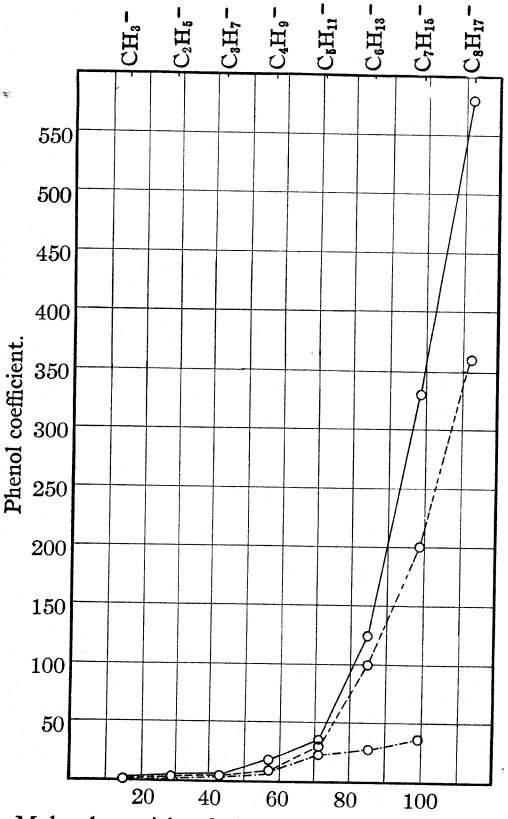



Fig. 2.—The effect of the molecular weight of the aliphatic radical on the bactericidal action of monoethers of dihydric phenols. Test organism, *Staph. aureus:* ——, resorcinol monoethers; – – –, hydroquinone monoethers; —·—·—, pyrocatechol monoethers.

The figures in Table III indicate that the three hydroxydiphenyl sulfides are more effective germicides than the corresponding oxides, when tested against *B. typhosus*.

The favorable effect of substitution by aliphatic and aromatic radicals upon the antibacterial action of phenols, has prompted us to take up the investigation of the antibacterial properties of substituted aromatic amines, phenol-ether amines and aminophenols; at this time we are in possession of some promising preliminary findings.

## Experimental Part

(a) **Chemical.**—The methods used in the preparation and purification of the pyrocatechol monoethers were essentially the same as those applied in the case of the resorcinol and hydroquinone monoethers, *i. e.*, pyrocatechol could be brought into reaction with the alkyl or alpharyl halides in the presence of potassium hydroxide or carbonate. It seems unnecessary to give a

detailed description of the methods used in preparing the pyrocatechol monoethers and separating them from the diethers produced simultaneously; it is sufficient to refer to the experimental parts of the preceding publications.

It is of interest, however, that the pyrocatechol monoethers are very readily volatile with steam, more so than the corresponding hydroquinone and resorcinol derivatives. This property facilitated the purification, and particularly the separation from unconverted pyrocatechol. The latter is somewhat volatile with steam, but can be removed from the distillate practically completely by simple decantation of the aqueous layer. Steam distillation was not applied in the case of the *n*-hexyl, *n*-heptyl and phenylpropyl ethers, since these compounds of comparatively high molecular weight do not distil over with sufficient rapidity.

Final purification was achieved by repeated distillation under reduced pressure and recrystallization wherever feasible.

Since the pyrocatechol monophenyl ether (*o*-hydroxydiphenyl oxide) was prepared by a different method, a complete statement of the experimental conditions is given below.

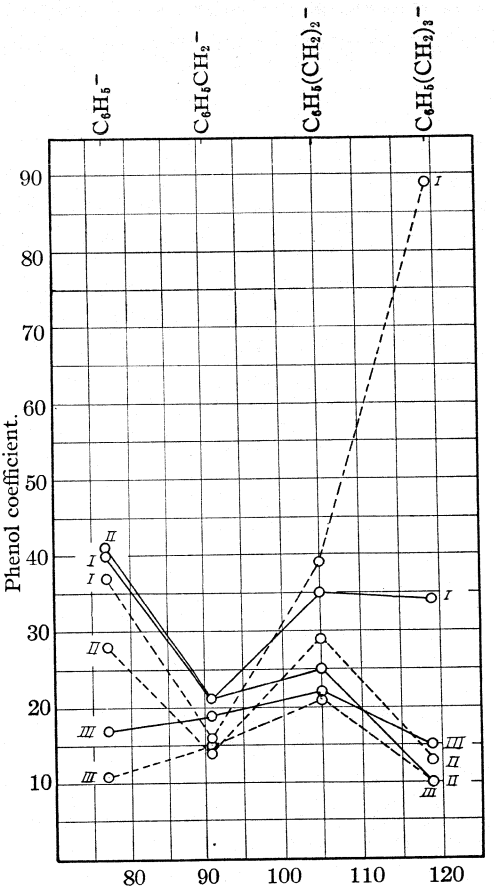



Fig. 3.—The bactericidal action of certain aromatic and alkyl-aromatic monoethers of dihydric phenols: I, resorcinol monoethers; II, hydroquinone monoethers; III, pyrocatechol monoethers. Test organisms: ——, *B. typhosus;* — — —, *Staph. aureus.*

**Preparation of *o*-Hydroxydiphenyl Oxide.**—Phenol (31 g.) and potassium hydroxide (22 g.) were mixed with a small amount of water to bring about complete solution, and heated in an oil-bath at about 150–160° until practically all the water was driven out. The solidified mass was finely ground and 57.7 g. of *o*-bromophenol and 0.3 g. of freshly reduced, finely subdivided, copper were added. The vessel was connected with a condenser and the mixture refluxed for six hours in an oil-bath with frequent shaking. The reaction product formed a heavy black oil. It was treated with water, acidified

and extracted with ether. The phenolic bodies were extracted with a 10% potassium hydroxide solution; the extract was acidified and subjected to steam distillation. At first a colorless oil came over consisting of a mixture of phenol and bromophenol; it was discarded. Then a white mass began to crystallize in the condenser. The distillation was continued until no more crystals collected in the distillate. The filtered crystalline product was dried and recrystallized from a mixture of benzene and petroleum benzene. The substance melted at 104°.

The analytical data of the pyrocatechol monoethers are given in Table IV.

TABLE IV

ANALYTICAL DATA

| | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | B. p. °C. | B. p. Mm. | M. p., °C. |
|---|---|---|---|---|---|---|---|---|
| **Aliphatic Ethers** | | | | | | | | |
| Ethyl | $C_8H_{10}O_2$ | 69.54 | 69.63 | 7.29 | 7.55 | 74–76 | 4 | .. |
| *n*-Propyl | $C_9H_{12}O_2$ | 71.01 | 71.22 | 7.96 | 8.17 | 80–83 | 4 | .. |
| *n*-Butyl | $C_{10}H_{14}O_2$ | 72.26 | 72.44 | 8.49 | 8.53 | 93–96 | 5 | .. |
| *n*-Amyl | $C_{11}H_{16}O_2$ | 73.31 | 73.00 | 8.95 | 8.74 | 104–106 | 4 | .. |
| *Sec.*-amyl | $C_{11}H_{16}O_2$ | 73.31 | 73.91 | 8.95 | 8.89 | 102–104 | 5 | .. |
| *n*-Hexyl | $C_{12}H_{18}O_2$ | 74.20 | 74.20 | 9.34 | 9.42 | 114–116 | 3.5 | .. |
| *n*-Heptyl | $C_{13}H_{20}O_2$ | 74.98 | 74.98 | 9.68 | 9.99 | 125–127 | 4 | .. |
| **Aromatic Ethers** | | | | | | | | |
| Phenyl | $C_{12}H_{10}O_2$ | 77.43 | 77.39 | 5.42 | 5.73 | ... | ... | 104[a] |
| Benzyl | $C_{13}H_{12}O_2$ | 78.01 | 77.44 | 6.05 | 6.27 | 157 | 6 | .. |
| Phenylethyl | $C_{14}H_{14}O_2$ | 78.48 | 78.61 | 6.59 | 6.83 | ... | ... | 48[b] |
| Phenylpropyl | $C_{15}H_{16}O_2$ | 78.92 | 79.04 | 7.07 | 7.48 | ... | ... | 51[c] |

[a] Recrystallized from a mixture of benzene and petroleum benzene.

[b] Recrystallized from 25% alcohol.

[c] Recrystallized from hexane and then from 25% alcohol.

(b) **Bacteriological.**—The method used in determining the germicidal action of the pyrocatechol derivatives studied was the same as that used in our work on the resorcinol and hydroquinone monoethers.

On the whole the monoethers of pyrocatechol were found to require an even greater proportion of alcohol in the minimum germicidal concentrations than the compounds of resorcinol and hydroquinone, with the exception of the *n*-heptyl and the phenylpropyl ethers. However, not more than 20% of alcohol was present in the final dilutions. The *n*-heptyl monoether required 40% of alcohol in the test with *B. typhosus* and 35% in that with *Staph. aureus;* the phenylpropyl monoether required 20 and 30% of alcohol, respectively.

## Summary

In continuation of the work on the bactericidal properties of monoethers of dihydric phenols, the following derivatives of pyrocatechol were studied bacteriologically: methyl (guaiacol), ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *sec.*-amyl, *n*-hexyl, *n*-heptyl; phenyl, benzyl, phenylethyl and phenylpropyl.

All pyrocatechol monoethers studied are bactericidal agents, but of varying potency, dependent upon the molecular weight and the structure of the substituting radical. While pyrocatechol is less effective than phenol, and guaiacol (its monomethyl ether) is practically as potent, the germicidal efficacy against *B. typhosus* increases with the increasing length of the aliphatic chain, reaching a maximum with the *n*-amyl ether and decreasing thereafter. With *Staph. aureus* no maximum is observed up to the *n*-heptyl ether. The *sec.*-amyl derivative is less effective in either case than the normal one. In the case of the aromatic ethers the maximum potency against both bacteria is shown by the phenylethyl ether.

The hydroquinone monoethers, with certain exceptions, are more effective bactericides than the corresponding pyrocatechol derivatives, while the resorcinol monoethers are generally the most potent. The higher mono-alkyl ethers of pyrocatechol do not reach the extraordinary heights of bactericidal action upon *Staph. aureus* shown by the corresponding resorcinol and hydroquinone ethers. The maximum effect upon *B. typhosus* in the series of hydroquinone and pyrocatechol monoethers is shown by the *n*-amyl ethers, while in the resorcinol series it is reached with the *n*-hexyl ether.

Preliminary results of experiments with other pathogenic microörganisms indicate that the bactericidal effect of the monoethers of the three dihydric phenols upon the Gram negative bacteria *B. coli* and *B. pyocyaneus* resembles those obtained with *B. typhosus*, from the quantitative point of view and also from that of the position of the maximum of germicidal potency. The results with the Gram positive *Streptococcus haemolyticus* follow those obtained with *Staph. aureus* very closely. *Vibrio cholerae* is found to be very susceptible to the action of certain of the compounds studied; as to the position of the maximum of germicidal action, however, there is more resemblance to the behavior of the Gram positive bacteria in spite of the negative Gram reaction of the cholera germ.

The comparison of the action upon *B. typhosus* of the three phenyl ethers (hydroxydiphenyl oxides) with that of the three hydroxydiphenyl sulfides reveals the bactericidal superiority of the latter.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# THE STUDY OF EXTREMELY WEAK ACIDS

BY J. B. CONANT AND G. W. WHELAND

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The purpose of this paper is to make a preliminary exploration of the possibility of a quantitative study of such extremely weak acids as enols, alcohols, derivatives of ammonia and phenylated hydrocarbons. It is well known that all these substances form salt-like sodium and potassium derivatives and that to some extent, at least, reactions of the following type take place in absolute ether

$$RH + R'K \longrightarrow RK + R'H$$

Following Brönsted's definition of an acid and base, we may regard the hydrogen compounds as very weak acids and the ions of the metallic derivatives as extremely strong bases. In principle there is little to distinguish the interaction of acetic acid and sodium phenolate in water from the action of triphenylmethane and $(CH_3)_2CKC_6H_5$ in absolute ether.

Although the acidic properties of the phenylated hydrocarbons and similar substances have been often discussed, the possibility of comparing the strengths of a number of such extremely weak acids does not seem to have been considered except in the recent paper of Wooster and Mitchell[1] which concerns reactions in liquid ammonia. Leaving aside the possibility of applying an electrochemical method, it is clear that a scale of acids of increasing strength could be prepared by studying metathetical reactions between salts and acids provided the degree of dissociation of all the salts is approximately the same. It would only be necessary to determine whether a reaction of the type given above proceeded from right to left or *vice versa* with each pair of acid and salt. Considerable information of this sort is already available. For example, the action of sodium ethyl on toluene produces sodium benzyl, which in turn gives up its sodium to diphenylmethane;[2] the acid strengths are thus $(C_6H_5)_2CH_2 > C_6H_5CH_3 > C_2H_6$. Wooster and Mitchell[1] used potassium amide in liquid ammonia to divide the weakly acidic hydrocarbons into two classes, according to whether or not the potassium compound would be stable in liquid ammonia. Recently Ziegler[3] has greatly increased our knowledge of organo-metallic compounds and their behavior in ether. He has studied a number of metathesis reactions particularly with potassium dimethylphenylmethyl which he showed to be the salt of a weaker acid than triphenylmethane. He has also studied the conductivity in pyridine of the potassium deriva-

[1] Wooster and Mitchell, THIS JOURNAL, **52**, 688 (1930).

[2] Schorigin, *Ber.*, **41**, 2723 (1908); Schlenk and Bergmann, *Ann.*, **464**, 21 (1928).

[3] Ziegler, Crössman, Kleiner and Schäfer, *ibid.*, **473**, 1 (1929); Ziegler and Bähr, *Ber.*, **61**, 253 (1928).

tives of a few triarylmethanes.[4] His results tend to support the assumption that underlies the present investigation—namely, that the degree of dissociation is approximately the same for the salts of a variety of very weak acids. The conductivities in pyridine of potassium triphenylmethyl and potassium trinitrotriphenylmethyl were very similar though the acid strength of the hydrogen compounds is very different. In ether the conductivities are very much less and change in an anomalous way with dilution, but there is no reason to believe that a change in solvent would affect seriously the relative degrees of dissociation of a series of related salts. Evidence pointing in the same direction has been obtained by Bent[5] in his study of the electron affinity of free radicals. His results indicated that the degree of dissociation of the sodium derivatives of the triarylmethanes he studied were the same within a power of ten. The quantitative study of very weak acids in such solvents as ether is undoubtedly greatly complicated by differences in the degree of dissociation of the salts, and differences may be expected in changing the solvent from ether to pyridine or liquid ammonia. The dissociation constants of the acids are thus to be interpreted with the reservation that they are somewhat uncertain due to variations in the activity of the negative ion. It should be pointed out, however, that the same situation holds, though probably to a less serious extent, in regard to the degree of dissociation of the usual weak acids determined in water solution.[6] Because of the variations of the constants relative to each other in going from one solvent to another, it is doubtful whether any significance can be attached to changes of two or three-fold in the dissociation constant with changes in structure.

We have chosen to use anhydrous ether as a solvent because of the high solubility in it of almost all the hydrogen compounds and nearly all the sodium or potassium derivatives. All the experiments were performed in a dry nitrogen atmosphere, of course. In Table I are collected the results of our preliminary survey of the situation. The hydrogen compounds are listed in the first vertical column and the corresponding sodium or potassium derivatives (*i. e.*, salts) across the top. Each square summarizes our experiments with a pair of compounds; the symbols used are explained in the attached key and the experimental procedure is given in the last part of this paper. Two methods were employed for determining whether or not a pair of compounds had interacted. The first method was to observe the color of the solution. The color of a number of the metallic compounds is very characteristic (top horizontal column, Table I), and the color changes therefore give definite information. The other method was to treat the reaction mixture with dry carbon dioxide and after a short

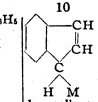
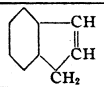
[4] Ziegler and Wollschitt, *Ann.*, **479**, 123 (1930).

[5] Bent, THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931).

[6] Halford, *ibid.*, **53**, 2939, 2944 (1931).

TABLE I

SUMMARY OF REACTIONS BETWEEN METHANE DERIVATIVES RH AND ORGANO-METALLIC COMPOUNDS (OF K OR Na) RM

| | | 1 $C_6H_5$ $(CH_3)_2$ CM | 2 $(C_6H_5)_2$·C :$CHCH_2M$ | 3 $(C_6H_5)_2CHM$ | 4 $(C_6H_5)_2$ $C_{10}H_7$ CM | 5 $(C_6H_5)_3CM$ | 6 $(C_6H_5)_2$ $C_6H_5C_6H_4$ CM | 7 O $C_6H_4$ $C_6H_4$ C H M | 8 $C_6H_4$ $C_6H_4$ C H M | 9 $C_6H_4$ $C_6H_4$ C $C_6H_5$ M | 10  | 11 $C_6H_5$· C : CM | 12 $C_6H_5C$ OM $CH_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | red | red brown | orange | green | orange red | purple | orange red | yellow | orange | 1. yellow | colorless | colorless |
| 1 | $C_6H_5$ $(CH_3)_2$ CH | | (−) | (−) | (−) | (−) | (−) | (−) | | (−) | | | (−) |
| 2 | $(C_6H_5)_2$·C:$CHCH_3$ | *K +C A | | (−) | K −C | K −C A | | | | | | | |
| 3 | $(C_6H_5)_2CH_2$ | K +C A | **K +C | | Na −C | Na −C | Na −C | | | | | | |
| 4 | $(C_6H_5)_2$ $C_{10}H_7$ CH | K +C A | **K +C | **K +C | | Na −C | Na −C | (−) | (−) | (−) | | (−) | (−) |
| 5 | $(C_6H_5)_3CH$ | K +C | | | K D Na | | Na −C | | (−) | (−) | (−) | (−) | (−) |
| 6 | $(C_6H_5)_2$ $C_6H_5C_6H_4$ CH | K +C | | | *K ***Na +C A | ***Na +C | | (−) | (−) | (−) | (−) | (−) | (−) |
| 7 | O $C_6H_4$ $C_6H_4$ $CH_2$ | *K +C | | | **Na +C | | **K **Na +C A | | (−) | | | | |
| 8 | $C_6H_4$ $C_6H_4$ $CH_2$ | | | | K +Na C | Na +C A | Na +C | K +C A | | Na −A | Na −A | | |
| 9 | $C_6H_4$ $C_6H_4$ C $C_6H_5$ H | K +C | | | K +C | Na +C | Na +C A | | Na +A | | Na E A | Na E A | |
| 10 |  | | | | | Na +C A | Na +C | | Na +A | Na E A | | Na E A | Na −A |
| 11 | $C_6H_5C$ : CH | | | | Na +C | Na +C A | Na +C | | | Na E A | Na E A | | |
| 12 | $C_6H_5COCH_3$ | K +C | | | Na K +C | Na +C | Na K +C | | | | Na +A | | |

EXPLANATION OF SYMBOLS IN TABLE

In each square is summarized the information in regard to the reaction between the methane on the left and the metallic compound at the top, in absolute ether in nitrogen; K or Na signify whether the K or Na salt (or both) was tried. The other

symbols have the following meaning: +, reaction goes essentially to completion; −, no evident reaction; E, incomplete reaction judged to be an equilibrium (the two squares joined by an arrow are the same experiment); (−), no reaction between these components since they are the products in a reaction going essentially to completion; D, decomposition instead of expected reaction; the letter C, and A, indicate whether the reaction was followed colorimetrically or by isolating the corresponding acid after treatment with carbon dioxide. In the first case a five-fold excess of hydrogen compound was employed, in the second equimolecular quantities of the reactants. Unless starred the reactions were instantaneous; the time necessary for practical completion in the other cases is noted as follows: *, a few hours; **, a few days; ***, about a month.

time treat with water and isolate the carboxylic acid in the usual manner. The reaction of all the metallic compounds (except No. 12) with carbon dioxide is very rapid. The validity of this method depends on the rate of the carbonation reaction being more rapid than the rate of metathesis; in some cases where the metathesis is very slow this assumption is certainly justified even if the metathesis is a balanced reaction containing a considerable amount of both salts. In other cases the assumption might be questioned. In the reactions involving indene and phenylacetylene, in which there seemed to be a measurable amount of both salts in the final reaction mixture, the amount of the two carboxylic acids isolated is a correct measure of the composition of the equilibrium only if both salts are carbonated before any shift of the equilibrium occurs. In every case where it was possible to use both the colorimetric and carbonation methods the results obtained by the two methods agreed.

The reaction between sodium or potassium α-naphthyldiphenylmethyl and triphenylmethane was the only anomalous one found. When the sodium salt was used, the solution decolorized through a dirty brown to the usual light yellow in a length of time varying erratically from a few minutes to several months. The following regularities, however, could be observed: the speed of decolorization increased with the temperature and with the concentration of triphenylmethane. When the potassium salt was used, decolorization was invariably almost instantaneous. In no case was the orange-red color of sodium or potassium triphenylmethyl formed, even momentarily. The source of the triphenylmethane apparently made no difference since two different samples from different sources showed the same behavior. The first sample was obtained from the Eastman Kodak Co., and was carefully purified before using by boiling for six hours with an equal weight of zinc dust in glacial acetic acid, and then recrystallizing from acetic acid. The second sample was prepared by the method of Reychler[7] from phenylmagnesium bromide and chloroform, and recrystallized from alcohol. Neither sample gave a yellow color with concentrated sulfuric acid (test for triphenylcarbinol) and both melted 93–94°. We have no explanation of the anomalous course of this reaction to propose.

[7] Reychler, *Bull. soc. chim.*, [3] **35**, 738 (1906).

All the results we have obtained are consistent with the idea that the different compounds listed in the first vertical column of Table I are acids of increasing strength, dimethylphenylmethane being the weakest and acetophenone the strongest; phenylacetylene, indene and phenylfluorene are of nearly the same strength. This list can undoubtedly be increased and by so doing it may be possible to find other compounds of sufficiently different acidity to place them between certain members of the present series. The more closely such a series of compounds overlaps the more service it will be in determining the relative strength of each new compound added to it. We are planning to continue this work in this direction. As an indication of the method to be employed we may cite the case of aniline. The acid strength of this compound may be roughly estimated by the following facts: aniline decolorizes an ethereal solution of potassium xanthyl but does not affect a solution of potassium fluoryl. Aniline therefore is of approximately the same acid strength as fluorene (certainly no stronger) and probably lies between this compound (No. 8) and xanthane (No. 7).

It is interesting to attempt to estimate the order of magnitude of the dissociation constants of these extremely weak acids, though, of course, no numerical values can be assigned with any certainty. If we define the acid strength ($pK$) by the usual equation, the difference in $pK$ values for two acids would be given by the following equation, in which the concentrations are those in the equilibrium mixture:

$$(pK)_1 - (pK)_2 = \log \frac{[R_1^-]}{[R_1H]} - \log \frac{[R_2^-]}{[R_2H]}$$

If we now assume that all the metallic salts with which we are concerned are approximately equally dissociated in ether solution we may substitute the concentration of the salts, $[R_1Me]$ and $[R_2Me]$ for the concentration of the ions in the above equation. (The salts are certainly very much more dissociated than the corresponding hydrogen compounds.) If no excess of the hydrogen compound was used in an experiment, we estimate that the metathesis $R_1H + R_2Me \longrightarrow R_1Me + R_2H$ will proceed to 90% completion if the acids differ by 2 $pK$ units. All the reactions indicated in Table I by a +, certainly were at least as complete as this but in the case of the colorimetric measurements about five-fold excess was employed, in which case a difference of 0.4 $pK$ units corresponds to 90% reaction. Therefore, we may conclude that the acid strengths of successive members in the series 1–8 differ by *at least* 0.4 or 2 $pK$ units depending on the nature of the experiment. As a starting point for our $pK$ scale we may take rather arbitrarily the value for acetophenone as 20 (since it is a weaker acid than ethyl alcohol[8] for which $K = 7 \times 10^{-20}$ (errors introduced by changes of solvent being neglected). The next three compounds higher on our list

[8] Danner, THIS JOURNAL, **44**, 2841 (1922).

(Nos. 11, 10, 9), are phenylacetylene, indene and phenylfluorene; these appear to be of nearly the same strength and since an experiment with equimolecular quantities shows that acetophenone is stronger than indene we may give a $pK$ value of 22 to the group. Similarly we may argue that there is a difference of 2 units between the $pK$ values of each of the next three compounds on our list (Nos. 8, 7, 6). The minimum value of diphenylbiphenylmethane (No. 6) is thus 28. Above this a minimum difference of 0.4 must exist between the successive members of the series since colorimetric experiments with a five-fold excess are the basis of the scale. The weakest acid on our list, dimethylphenylmethane (No. 1), thus has an estimated minimum $pK$ of 30.5–31. If one tries to interpret this large number with a kinetic picture of the degree of dissociation of the hydrocarbon into protons and negative ions, the result is probably meaningless. If one regards the value as the measure of an escaping tendency of protons, however, it has just as much meaning as very small values of vapor pressures obtained by extrapolation of data obtained at higher temperatures.

Weaker acids than the ones at the top of our list certainly are known, but their sodium and potassium salts are decomposed by ether. The work of Schorigin, Schlenk[2] and others indicates that toluene is weaker than diphenylmethane (whose value we estimate at 29.5), while ethane is still weaker than toluene. This would indicate a $pK$ value for ethane of perhaps 34, though it seems likely that this number is much too small.

When this work was first started it was a matter of great interest to us to see whether all the metathetical reactions were practically instantaneous, as they are with stronger acids in water and alcohol. It was soon found that this was not the case. The stars in the squares of Table I indicate the slow reactions; some of these require months at room temperature (indicated by * * * in Table I). No case of a slow reaction has been found with compounds more acidic than xanthane. However, there is no real parallelism between the rates and acidic strength since the potassium derivative of the weakest acid reacts rapidly with the next four acids in the series (Nos. 2, 3, 4, 5). One fact might indicate that the potassium derivatives react more rapidly than the sodium (6 + 4, Table I). This would be of considerable practical importance since if it takes months or even days for equilibrium to be established in a reaction between an acid and a salt, the usual methods of handling such reactions are materially altered.

Before this difference between the potassium and sodium salts was discovered some time was devoted to a quantitative study of the rates of two reactions which could be followed roughly by colorimetric comparison. These reactions were (1) between diphenylbiphenylmethane and sodium triphenylmethyl and (2) between xanthane and sodium diphenylbiphenylmethyl, both in dry ether. A considerable excess of the hydrogen com-

pound was taken in each case. Colorimetric standards were made from mixtures of the two sodium salts which would be present in the reaction mixture and the rate estimated by matching the reaction mixture against the standard. This crude method yielded surprisingly good results, bimolecular constants calculated from 12 to 50% conversion for reaction 1 and 50 to 90% for reaction 2 agreed within ±10%. The average values are given in Table II together with the heats of activation calculated from the temperature coefficient of the reaction. Because of the errors in the method, the values are uncertain by ±540 calories for reaction 1, and ±800 cal. for reaction 2.

TABLE II

| Reaction 1 | | | Reaction 2 | | |
|---|---|---|---|---|---|
| Concn. hydrogen cpd. 0.167 *M* | | | Concn. hydrogen cpd. 0.167 *M* | | |
| Concn. sodium cpd. 0.017 *M* | | | Concn. sodium cpd. 0.015 *M* | | |
| Temp., °C. | Approx. *k* | *E* | Temp., °C. | Approx. *k* | *E* |
| 25 | 0.0029 | 13,300 cal. | 0 | 0.29 | 13,800 cal. |
| 78 | .080 | (calcd. from | 25 | 2.2 | (calcd. from |
| 100 | .21 | 25° to 110°) | 42 | 8.6 | 0 to 42°) |
| 110 | .41 | | | | |

$k = \frac{1}{t} \cdot \frac{2.3}{b-a} \log \frac{a(b-x)}{b(a-x)}$ where $t$ is time in hours, $a$ and $b$ initial concentrations of reactants, and $x$ concentration of product.

## Experimental

Considerable difficulty was encountered in designing a storage flask for keeping the solutions of the metallic derivatives and a number of unsuccessful types were used and discarded before a really satisfactory one was developed. The difficulty lay in the fact that it was apparently impossible to find a grease for the stopcock through which the solution was to be drawn off which would hold against ether and at the same time not react with the metallic derivatives. If a vaseline–rubber grease were used the stopcock would leak so badly after having been opened once that air would enter the flask and decompose the metallic derivative in a few hours, while on the other hand if one of the ether-insoluble greases were used, the solution would be decolorized on passing through the stopcock. The problem was finally solved by using a vaseline–rubber grease which was inert toward the metallic derivatives, and by protecting the stopcock with a mercury seal. The apparatus consisted of a 200-cc. flask in which the metallic derivative was prepared and a roughly graduated buret attached as a side arm, much as described by Ziegler.[9] The stopcock in this buret was three-way, one opening leading to the vessel to be filled, the other connected with a small reservoir of mercury. When the buret was closed the mercury was admitted into the bottom, making a layer of a few millimeters which sealed the opening effectively. The tubes which were filled from this buret were arranged so that they could be evacuated and filled with oxygen-free dry nitrogen.

The method of preparing the metallic compounds depended somewhat on the nature of the compound. The potassium and sodium derivatives of diphenyl-α-naphthylmethane, triphenylmethane and diphenylbiphenylmethane (Nos. 4, 5, 6)

[9] Ziegler, Crössmann, Kleiner and Schäfer, *Ann.*, **473**, 20–21 (1929).

were prepared by the action of sodium or potassium amalgam (sufficiently dilute amalgams to be liquid) on the corresponding chlorides in dry ether in nitrogen. The reaction here is really the formation of the free radical followed by the addition of alkali metal to the radical. The potassium derivatives of phenyldimethylmethane and xanthane (1 and 7) were prepared by the action of sodium–potassium alloy on the corresponding ether[10] in the one case and the cleavage of dixanthyl with the same reagent in the other. In some cases an indirect procedure was employed in which the metallic derivative of a less acidic substance was allowed to react with the compound. Such a method was used in preparing the potassium derivative of 1,1-diphenyl-2-methylethylene (No. 2), the potassium derivative of phenyldimethylmethane being allowed to react with a slight excess of the compound. The potassium derivative is a reddish brown substance only slightly soluble in ether. In the preparation of sodium fluoryl (No. 8) sodium phenylfluoryl (No. 9), sodium indyl (No. 10) and sodium phenylacetylide (No. 11), the method was slightly modified by breaking a capsule of the hydrocarbon in a reaction mixture containing sodium triphenylmethyl prepared from the chloride and sodium amalgam (all in dry ether and nitrogen, of course).

**Standardization of Solutions.**—Three different methods were used for standardizing the solutions of the various metallic derivatives. (a) Three cc. of the solution was run into water and the resulting alkali was then titrated with standard acid. (b) One drop of acetophenone from a calibrated dropping-tip was titrated with the solution until the formation of a permanent color. (c) A measured volume of a standard solution of benzoic acid in dry benzene was titrated with the solution until the formation of a permanent color. These methods were not particularly accurate, but, in consideration of the roughness of the work, they were quite satisfactory. The three different methods agreed with each other as well as any one method agreed with itself, *i. e.*, to within possibly 10–15%.

**Identification of Metallic Compounds.**—The identity of each of the metallic derivatives (except the one from acetophenone) was confirmed by treating the ethereal solution with dry carbon dioxide and isolating the carboxylic acid in the usual way. The yields of pure crystalline acid were 40–70%. The acids were for the most part known substances and their melting points (in some cases supplemented by their titration equivalents) served to identify them.[11] The following acids were new compounds and were analyzed as free acids and esters.

**α-Naphthyldiphenylacetic Acid.**—The yield of acid was 40% of the theoretical when dry carbon dioxide was allowed to act on the sodium derivative prepared from α-naphthyldiphenylmethyl chloride and sodium amalgam in dry ether. The compound melted at 240°.

*Anal.* Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.33; equiv. wt., 338. Found: C, 85.3, 84.9; H, 4.98, 4.73; equiv. wt. (by titration with sodium hydroxide, phenolphthalein indicator), 395.

**Methyl Ester of α-Naphthyldiphenylacetic Acid.**—The acid was esterified by dissolving in a small amount of 10% sodium hydroxide and boiling with an excess of dimethyl sulfate. The product was recrystallized from methyl alcohol; it melted at 189–191°.

*Anal.* Calcd. for $C_{25}H_{20}O_2$: C, 85.2; H, 5.73; mol. wt., 352. Found: C, 84.8; H, 5.82; mol. wt. (freezing benzene), 348, 332.

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[10] Ziegler and Schnell, *Ann.*, **437**, 255 (1924).

[11] The acid obtained from sodium fluoryl melted at 223–224° and had an equivalent weight by titration of 218 (theoretical 210). These results confirm those of Kliegl [*Ber.*, **62**, 1328–9 (1929)].

**Biphenyldiphenylacetic Acid.**—A 70% yield of this acid was obtained from the corresponding sodium derivative and carbon dioxide. The compound melted at 220–222°.

*Anal.* Calcd. for $C_{26}H_{20}O_2$: C, 85.7; H, 5.53; equiv. wt. 364. Found: C, 85.5; H, 5.69; equiv. wt. (by titration with sodium hydroxide) 368.

**Methyl Ester of Biphenyldiphenylacetic Acid.**—The ester was prepared by the action of dimethyl sulfate on an aqueous solution of the sodium salt of the acid; it melted at 170°. *Anal.* Calcd. for $C_{27}H_{22}O_2$: C, 85.7; H, 5.86; mol. wt., 378. Found: C, 85.4; H, 5.90; mol. wt. (benzene), 375, 390.

**Procedure for Following Reactions.**—All of the colorimetric reactions, with the exceptions noted below, were carried out in the following manner. A weighed quantity of the hydrocarbon (usually a several-fold excess) was placed in a carefully cleaned and dried 14 × 120 mm. test-tube which was then drawn down to a thick-walled capillary and attached to the buret side arm of the storage flask; 3 cc. of the solution was then run out into the tube after the latter had been evacuated and filled with nitrogen and the tube was sealed off at the constriction. The hydrocarbon was brought into solution by shaking for a few minutes, and the tube was observed from time to time to see if any color change took place. In the case of those reactions which took place instantaneously, the drawing down and subsequent sealing off of the tube were of course unnecessary.

A special procedure was employed in those cases where the metallic derivatives were so insoluble that they precipitated. A 14 × 120 mm. test-tube with bent sealed-off side-arm was cleaned and dried as before. The more acidic hydrocarbon was placed in the small side-arm, the less acidic one in the larger tube, which was then drawn down to a capillary. After 3 cc. of potassium phenylisopropyl solution had been introduced into this tube in the usual manner, the tube was sealed off at the constriction. Inside of an hour or so, the solution had turned to the color of the potassium salt of the hydrocarbon placed originally in the wider tube and a heavy precipitate of the metallic derivative had formed. The tube was then tipped so as to wash out the side arm and thus bring the second hydrocarbon into solution. In the course of several days the color of the solution and of the precipitate changed slowly to that of the potassium salt of the second (more acidic) hydrocarbon.

Since solubility effects enter into these reactions, the acid strengths of the hydrocarbons are not the only factors involved. Thus, the order of the acid strengths and the estimated minimum $pK_a$'s are not so definitely established here as in the other cases, but it is doubtful whether this very seriously affects the validity of the results. These complications occurred only with diphenylmethane and diphenylmethylethylene, whose potassium or sodium derivatives were very little soluble in ether.

If the metallic derivatives had to be prepared indirectly and if the reaction took place instantly, a third procedure had to be employed. This procedure was used with sodium fluoryl, sodium phenylfluoryl, sodium indyl, sodium phenylacetylide and the sodium derivative of acetophenone. The two hydrogen compounds to be compared were sealed off under nitrogen in thin-walled capsules, which were then broken in a solution of sodium triphenylmethyl. The hydrocarbons thus competed for the sodium furnished by the metallic derivative, and since the reactions took place instantly there can be no doubt that equilibrium was reached almost at once, with the stronger acid in possession of the sodium. The reaction mixture was then treated with carbon dioxide and the resulting acid was isolated and identified in the usual way. Since some of the reactions yielded a mixture of acids, a summary of the experimental results in these cases is given below.

Fluorene and indene were treated together with sodium triphenylmethyl solution, and then carbon dioxide yielded indene-3-carboxylic acid in a 50% yield. Phenyl-

fluorene and fluorene under the same conditions gave a 60% yield of 9-phenylfluorene-9-carboxylic acid. In both of these cases the crude acids appeared to be quite pure. They were identified by mixed melting point determinations and by determining the equivalent weight by titration with alkali. When phenylfluorene and phenylacetylene were used, however, the isolated acid was clearly a mixture. The equivalent weight (by titration) was found to be 181 (calcd. for phenylacetylene acid 146, for the fluorene derivative 286). The mixture was separated by fractional crystallization into the pure fluorene acid (identified by mixed melting points and equivalent weight determinations), and an impure phenylpropiolic acid. Similarly phenylfluorene and indene yielded a crude acid (first separating as an oil) melting at 90–100° with an equivalent weight of 217 (calcd. for the phenylfluoryl acid 286, for the indene acid, 160). Phenylacetylene and indene also yielded a mixture of acids as judged by the melting point 95–105°. The equivalent weight determination is here of little value; the calculated equivalent weights are 160 and 146; the value found was 161.

## Summary

1. The interaction of twelve extremely weak acids and the corresponding sodium or potassium compounds has been studied in anhydrous ether. From the results of these metatheses, it is possible to arrange the acids in a scale of increasing strength. The use of this scale in estimating the strength of other very weak acids is illustrated by a consideration of aniline.

2. The rates of interaction of certain phenylated hydrocarbons and the corresponding sodium derivatives have been estimated at several different temperatures.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

# ALIPHATIC AMMONO ALDEHYDES[1]

BY HAROLD H. STRAIN

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The aromatic imines, hydramides and Schiff's bases undergo many reactions which support the view that these substances are aldehydes of an ammonia system of compounds.[2] It is to be expected, therefore, that similar aliphatic nitrogen compounds should exhibit reactions characteristic of aliphatic aldehydes.

A search of the literature revealed to our surprise that but few aliphatic imines and hydramides are known. Subsequent experiments demonstrated that conditions conducive to the formation of aromatic ammono aldehydes did not necessarily promote the formation of the corresponding aliphatic compounds. Our present knowledge of the occurrence of the common aliphatic ammono aldehydes is summarized in Table I.

[1] Original manuscript received May 19, 1930.

[2] (a) Franklin, THIS JOURNAL, **46**, 2137 (1924); (b) Strain, *ibid.*, **49**, 1558 (1927); (c) **50**, 2218 (1928); (d) **52**, 1216 (1930); (e) **51**, 269 (1929).

TABLE I

ALIPHATIC AMMONO ALDEHYDES*

| Aldehyde | Imine | Hydramide | Schiff's bases |
|---|---|---|---|
| Formaldehyde[a] | Unknown | Unknown | Known |
| Acetaldehyde[b] | Known | ? | Known |
| Chloral[c] | Known | Unknown | Known |
| Propionaldehyde[d] | Unknown | Unknown | Known |
| Butyraldehyde[e] | Unknown | Unknown | Known |
| Isobutyraldehyde[f] | ? | Known | Known |
| Heptaldehyde[g] | Unknown | ? | Known |

* Compare Beilstein, "Handbuch der organischen Chemie," 4te. Aufl. Bd. I: [a] p. 583; [b] p. 607; [c] p. 624; [d] p. 630; [e] p. 663; [f] p. 674; [g] p. 697.

All the aliphatic ammono aldehydes, particularly the Schiff's bases, undergo characteristic aldehyde reactions such as hydrolysis to the corresponding aquo aldehydes and formation of addition compounds with bisulfites and hydrocyanic acid.[2] Aliphatic Schiff's bases also form condensation products[3] which we regard as ammono aldol-acetals, as shown by the following equation.[4]

$$2CH_3CH{=}NC_6H_5 \longrightarrow \begin{matrix} CH_3CH{-}NHC_6H_5 \\ | \\ CH_2CH{=}NC_6H_5 \end{matrix}$$

Ammono aldehyde-acetal — Ammono aldol-acetal

In addition to the known reactions of the aliphatic imines, hydramides and Schiff's bases we have found that such substances undergo ammonolysis, reduction, nitridation, polymerization, depolymerization and condensation reactions. These reactions support the view that such substances are aliphatic ammono aldehydes.

When aldehyde ammonia is heated[5] or when aldehydes and alcoholic ammonia are heated,[6] pyridine derivatives are formed, particularly the 2,3,5-trisubstituted pyridines. Thus aldehyde ammonia forms 2-methylpyridine; propionaldehyde, 2-ethyl-3,5-dimethylpyridine; and butyraldehyde, 2-propyl-3,5-diethylpyridine. The formation of these substances may be explained reasonably as follows, assuming a complex ammono aldol to be formed which subsequently loses ammonia and hydrogen.

$$CH_3CH_2CH{=}NH + CH_3CH_2CH{=}NH = \begin{matrix} CH_3CH_2CH{-}NH_2 \\ | \\ CH_3CHCH{=}NH \end{matrix}$$

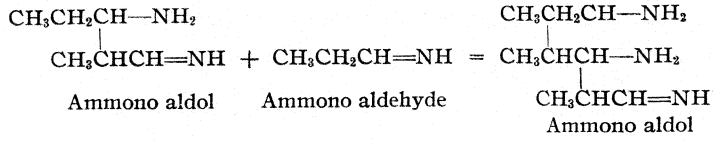
Ammono aldehyde — Ammono aldehyde — Ammono aldol

[3] (a) Schiff, *Ann., Suppl.*, **3**, 343 (1864); (b) Miller, Plöchl and Eckstein, *Ber.*, **25**, 2029 (1892); (c) Miller, *ibid.*, **25**, 3072 (1892); (d) Schiff, *Ann.*, **140**, 129 (1866); *ibid.*, **210**, 127 (1881).

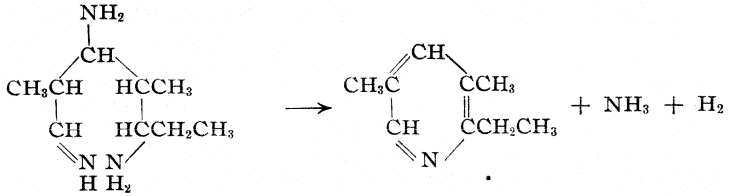
[4] These substances are ammono aldol-acetals in the same sense that the analogous aromatic compounds are ammono benzoin-acetals.[2e]

[5] Dürkopf and Schlaugk, *Ber.*, **21**, 297 (1888).

[6] (a) Waage, *Monatsh.*, **4**, 724 (1883); (b) Dürkopf and Göttsch, *Ber.*, **23**, 685 (1890); (c) Tschitschibabin, *Chem. Zentr.*, [I] **77**, 1439 (1906); (d) Schiff, *Ann., Suppl.*, **3**, 343 (1864).




Ammono aldol Ammono aldehyde Ammono aldol




Ammono aldol 2-Ethyl-3,5-dimethylpyridine

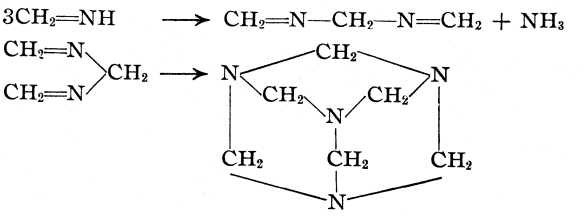
Experimental evidence indicates that aquo ammono aldols containing one oxygen atom rather than ammono aldols are intermediates in this reaction. As will be shown in the experimental part the higher normal aliphatic aldehydes react with liquid ammonia to form aquo ammono aldols rather than imines or hydramides. It should be pointed out, however, that these aquo ammono aldols may contain nitrogen and oxygen in variable proportions and in different positions in the molecule, depending upon whether aquo or ammono aldehydes first enter the reaction. Further support of this reaction mechanism is afforded by the reaction of isobutyraldehyde in liquid ammonia. As is well known, isobutyraldehyde resembles the aromatic aldehydes in that it undergoes intermolecular oxidation and reduction when treated with alkalies (Canizzaro reaction). Accordingly one should expect this substance to form an imine or an hydramide in liquid ammonia solution rather than an aldol and such has been found to be the case. Although the above mechanism indicates that hydrogen should be produced, we have been unable to detect it. Whether the aldols or dihydropyridines are dehydrogenated by complex organic compounds present in the mixture is problematical.

## Experimental

**Methylene Imine.**—Reactions which should lead to the formation of methylene imine invariably produce hexamethylenetetramine.[7] According to Franklin [2a] this reaction probably takes the following course[8]

[7] Butlerow, *Ann.*, **116,** 322 (1860); Höland, *Ann.*, **240,** 225 (1887).

[8] Many reactions, as well as the crystal analysis, support the structure given above for hexamethylenetetramine [Duden and Scharff, *Ann.*, **288,** 218 (1895); Dickinson and Raymond, THIS JOURNAL, **45,** 22 (1923)] which is to be regarded as a polymerized ammonoformaldehyde. Nevertheless a few investigators [Harvey and Baekeland, *Ind. Eng. Chem.*, **13,** 134 (1921); Marotta and Alessandrini, *Gazz. chim. ital.*, **59,** 942 (1929)] believe certain reactions indicate the presence of double bonds in the molecule. Yet it should be noted that such reactions are always carried out in the presence of solvents or reagents which cause the depolymerization or solvolysis of the hexamethylenetetramine. If hexamethylenetetramine does contain double bonds,



In view of the fact that benzylidene imine is stable in liquid ammonia solution,[2b] attempts to prepare methylene imine from methylene chloride in liquid ammonia solution were made with the surmise that the free imine might not lose ammonia to form hexamethylenetetramine. The methylene chloride, which was only slightly soluble in liquid ammonia at room temperature, showed no sign of reacting after standing for 24 hours. Upon heating the solution to 180° for two hours the methylene chloride dissolved, forming hexamethylenetetramine which separated from the solution in large colorless crystals. These crystals are only slightly soluble in liquid ammonia at room temperature.

**Hexamethylenetetramine.**—In trying to depolymerize hexamethylenetetramine we passed the vapors through an evacuated glass tube which was heated to redness without producing any change. Soda-lime placed in the tube caused no depolymerization or decomposition to take place. Dilution of the vapors with ammonia gas also proved to be without effect.

When hexamethylenetetramine is heated with liquid ammonia at 210° for eighteen hours no ammonation takes place, although the small crystals which are used originally are converted into large hexagonal crystals which decrepitate upon heating or upon dissolving in water and alcohol. The addition of aniline or potassium amide to the solution does not cause reaction to take place during the heating.

Hexamethylenetetramine is not nitridized by a solution of iodine in liquid ammonia at −33°, nor by hydrazoic acid in liquid ammonia at 260–270° for twelve hours. The marked stability of hexamethylenetetramine toward metallic nitrides has been reported by Schurman and Fernelius.[9]

**Anhydroformaldehyde Aniline.**—Anhydroformaldehyde aniline (ammono formaldehyde-acetal) is but slightly soluble in liquid ammonia at room temperature. It is nitridized very slowly by a solution of iodine in liquid ammonia at −33°.

When anhydroformaldehyde aniline is permitted to stand in contact with liquid ammonia at room temperature for thirty-five days no reaction takes place. The addition of ammonium chloride to the solution is also without effect. On the other hand, 3.0 g. of the ammono aldehyde-acetal, 1 g. of ammonium chloride and 15 cc. of liquid ammonia were found to react when heated to 150–180° for twelve hours, producing a clear solution. When cooled and agitated this solution deposited 0.3 g. of transparent hexagonal crystals which proved to be hexamethylenetetramine. The free aniline in the mother liquor was identified by the furfural test.

**Ethylidene Imine.**—Delépine[10] reports that acetaldehyde ammonia is converted into ethylidene imine when permitted to stand over sulfuric acid in a desiccator evacu-

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then it should be hydrogenated with colloidal platinum and hydrogen. As a matter of fact, the writer was unable to effect such a reduction in aqueous or absolute alcohol solution using Adams' catalyst and hydrogen pressure of four atmospheres [*cf.* Pummerer and Hofmann, *Ber.*, **56**, 1255 (1923)].

[9] Schurman and Fernelius, THIS JOURNAL, **52**, 2425 (1930).

[10] Delépine, *Ann. chim.*, [7] **16**, 103 (1899).

ated with a water pump. He also demonstrated that ethylidene imine thus prepared was a trimer which could be completely dissociated by heating to 260°. The formation of ethylidene imine may be regarded as the dehydration of aquo ammono ortho acetaldehyde to ammono acetaldehyde while the polymerization and depolymerization of ethylidene imine is analogous to the formation and dissociation of paraldehyde.

Although Delépine does not state the exact pressure at which he dehydrated aldehyde ammonia, we have found that dehydrations performed at different pressures yield quite different results.[11] When the pressure is very low (less than 1 mm.), all the aldehyde ammonia volatilizes and is absorbed by the sulfuric acid. At slightly higher pressures (1–10 mm.) large cube-shaped, transparent crystals of ethylidene imine are formed but the yields are small (5–25%). At a pressure of 3 cm. a nearly quantitative yield of ethylidene imine is obtained in two to three days, particularly if the depth of the layer to be dehydrated is not over 1–2 cm. The crystals obtained at this pressure are small and opaque. They are readily soluble in pyridine, forming a clear solution. The crystals dissolve in cold glacial acetic acid forming a light yellow solution which becomes quite dark in color upon standing or upon gentle warming.

Because of the ease with which aldehyde ammonia is dehydrated with sulfuric acid we concluded that ethylidene imine should be formed when aldehyde ammonia is treated with a dehydrating agent in liquid ammonia. Although potassium amide caused the formation of dark condensation products, calcium amide was found to serve as a suitable dehydrating agent. The ethylidene imine is obtained in large transparent crystals by evaporating the ammonia solution after it has been decanted from the slightly soluble calcium hydroxide and excess calcium amide.

Monomolecular ethylidene imine was obtained as a clear mobile liquid at room temperature by heating the trimolecular form to 260°, then suddenly cooling the vapors. This reaction was accomplished by placing the polymerized compound in a glass bulb which was in turn connected to another bulb by means of a glass tube about 28 cm. long so arranged that the connecting tube could be heated to 260–270° while the receiver was immersed in liquid ammonia. After evacuating and sealing the system, the ethylidene imine was heated until it volatilized, when it slowly distilled through the hot tube, condensing as a clear mobile liquid in the cold receiver. This liquid failed to crystallize when seeded with the original crystals. After standing for several hours (sometimes several days were necessary) the liquid slowly polymerized to the crystalline trimmer. By alternately heating and cooling the bulbs of the apparatus the depolymerization could be repeated as often as desired. During the heating process no ammonia was liberated, indicating that monomolecular ethylidene imine does not lose ammonia to form hydracetamide, a reaction which one would predict from the behavior of benzylidene imine.[2b]

A solution of ethylidene imine in liquid ammonia was treated with an excess of iodine and the temperature maintained at 0° until the iodine color had completely disappeared. The clear solution was then evaporated to dryness and the residue taken up in water. This aqueous solution deposited a yellow picrate melting at 244–245°, the melting point of acetamidine picrate, when treated with an aqueous solution of picric acid. Attempts to identify cyanethine as a nitridation product of ethylidene imine were fruitless.

Ethylidene imine reacts with malonic acid in hot pyridine with the evolution of carbon dioxide just as aquo aldehydes do. This ammono acetaldehyde also reacts with 2,4-dinitrophenylhydrazine in anhydrous pyridine or alcohol to form acetaldehyde 2,4-dinitrophenylhydrazone and ammonia.

[11] A good grade of aldehyde ammonia is easily obtained by recrystallizing commercial aldehyde ammonia from propyl or isopropyl alcohol.

**Hydracetamide.**—Both Schiff[12] and Strecker[13] found that an amorphous substance was produced when aldehyde ammonia was permitted to stand for long periods. Although the writer made many attempts to prepare this substance, no evidence for the formation of a pure compound was obtained. Pure aldehyde ammonia was found to be stable over long periods especially when preserved in sealed vessels in the dark. The ability of ethylidene imine to withstand heating without losing ammonia to form hydracetamide has already been commented on.

**Propionic Aldehyde.**—By heating propionaldehyde with ammonia,[6a] ammonium chloride,[14] or propionaldehyde ammonia[6b] 2-ethyl-3,5-dimethylpyridine has been obtained. That this reaction is dependent upon the formation of an intermediate aquo ammono aldol is shown by the following experiments.

Freshly distilled propionaldehyde was dissolved in liquid ammonia at room temperature and treated with a large excess of calcium amide. After twenty to thirty minutes the clear solution was decanted from the calcium hydroxide and excess calcium amide. The solvent was evaporated and the residue dried at 35° and 1 mm. pressure. The product was a colorless transparent viscous liquid.

*Anal.* Found: C, 64.0, 62.6; H, 12.3, 11.7; N, 18.4.

A second preparation in which the calcium amide treatment was omitted resulted in the formation of a similar viscous liquid.

*Anal.* Found: C, 62.6, 62.9; H, 11.7, 11.9; N, 16.8, 16.5.

| Calcd. for | C, % | H, % | N, % |
|---|---|---|---|
| $CH_3CH_2CH{=}NH$ | 63.2 | 12.3 | 24.5 |
| $(C_3H_6)_3N_2$ | 70.1 | 11.7 | 18.2 |
| $CH_3CH_2CH(OH)NH_2$ | 48.0 | 12.0 | 18.7 |
| $C_9H_{20}ON_2$ | 62.8 | 11.6 | 16.3 |

Both of the above products failed to produce propionaldehyde when warmed with aqueous hydrochloric acid. Upon distillation they decomposed, forming water, ammonia, and a high boiling substance. The absence of hydrogen was proved by distilling the preparations in a current of carbon dioxide, which was absorbed in dilute alkali. After two distillations a small quantity of material boiling at 195–200° was obtained; yields about 12%. A portion from each preparation formed a mercuric chloride compound which melted at 116–120°. The mercuric chloride compound of 2-ethyl-3,5-dimethylpyridine melts at 117–119°.[6b] The remaining portions from each high boiling fraction were combined and oxidized with a slight excess of 2% potassium permanganate solution at 60° for three days. After separating the manganese dioxide the acids in the filtrate were precipitated with copper sulfate. The copper salts were decomposed with hydrogen sulfide and after boiling and neutralization with sodium carbonate the acids were converted into the slightly soluble silver salts. After decomposing the silver salts with hydrogen sulfide, the solution was evaporated to dryness and the residue dissolved in the least possible quantity of hot water. Upon cooling crystals were obtained which melted at 316–318°. The melting point of pyridine 2,3,5-tricarboxylic acid is given as 318°[6b] and 323° with dec.[6c]

**Butyric Aldehyde.**—Butyric aldehyde reacts with liquid ammonia to form a slightly soluble clear viscous liquid and water. Calcium amide added to the solution removes the water but is apparently without effect upon the slightly soluble product. The solvent was evaporated and the product dried for two hours at 35° under 1 mm. pressure.

[12] Schiff, *Ann., Suppl.*, **6**, 1 (1868).

[13] Strecker, *ibid.*, **6**, 255 (1868).

[14] Plöchl, *Ber.*, **20**, 722 (1887).

*Anal.* Calcd. for $C_{12}H_{26}ON_2$: C, 67.3; H, 12.1. Found: C, 66.8, 66.8; H, 12.4, 12.4.

The material was not hydrolyzed to butyraldehyde when heated to 60° with 6 *N* hydrochloric acid. When distilled it formed water and ammonia (no hydrogen was formed) as well as a high boiling liquid. The latter, after two distillations, boiled at 245–250° at 763 mm.; yield 30%. Its density was 0.914 at 20°. It was soluble in aqueous hydrochloric acid but was not decomposed. Oxidized with 2% potassium permanganate at 60° for three and one-half days as described for the analogous compound obtained from propionaldehyde, we obtained a crystalline acid which melted at 317°. It is to be concluded that an aquo ammono aldol was formed which upon distillation gave rise to 2-propyl-3,5-diethylpyridine. The latter compound was obtained by Tschitschibabin upon heating butyraldehyde and alcoholic ammonia to 150° for fifty hours.[6c]

**Isobutyraldehyde.**—Isobutyraldehyde reacts with liquid ammonia to form a moderately soluble clear liquid. This liquid is much more mobile than the corresponding compounds obtained from butyraldehyde and unlike the latter it is rapidly hydrolyzed to isobutyraldehyde by dilute hydrochloric acid. A preparation which had been dried at −35° at 1 mm. pressure indicated the presence of ammonia or isobutylidene imine.

*Anal.* Calcd. for $C_3H_7CH{=}NH$: C, 67.6; H, 12.7; N, 19.7. Calcd. for $(C_3H_7CH{=})_3N_2$: C, 73.4; H, 12.2; N, 14.3. Found: C, 70.0, 70.2; H, 12.4, 12.4; N, 17.0.

Dried at 45° and 0.5 mm., the analysis approximated that of hydroisobutyramide.

*Anal.* Found: C, 73.0, 73.1; H, 12.0, 11.8; N, 14.0.

When heated rapidly the compound distilled at 150–155° at 760 mm. As its analysis was unchanged, it was evidently the same hydroisobutyramide isolated by Lipp as the distillation product of a compound $C_{28}H_{62}ON_6$ obtained in turn by the action of concentrated aqueous ammonia upon isobutyraldehyde.[15]

**Heptaldehyde.**—Heptaldehyde reacts with liquid ammonia to form a slightly soluble, viscous compound which is not hydrolyzed to heptaldehyde by aqueous acids. The analyses of this oil, dried at 45° at 1 mm., indicate the formation of an aquo ammono aldol.

*Anal.* Calcd. for $C_{21}H_{44}ON_2$: C, 74.1; H, 12.9; N, 8.2. Found: C, 73.8, 73.5; H, 12.6, 12.7; N, 8.5.

A similar liquid was obtained when an ether solution of heptaldehyde was saturated with ammonia. Both preparations gave off water and ammonia when distilled. The organic portion of the distillate boiled at 355–365°. This material was but slightly soluble in aqueous hydrochloric acid and was not hydrolyzed by the latter, indicating that it was not an hydramide as postulated by Schiff.[3] It was stable in liquid ammonia over long periods. It also failed to dissolve in a solution of potassium amide in liquid ammonia with the evolution of hydrogen, a reaction characteristic of aromatic hydramides.[2d] If heptaldehyde is analogous to propionic and butyric aldehydes in its reactions, we should expect this high-boiling compound to be 2-hexyl-3,5-dipentylpyridine. The reactions described above as well as the analysis support this structure. For analysis a 15-g. portion was distilled five times, each time the first and last 1 g. portions being discarded.

*Anal.* Calcd. for $C_{21}H_{37}N$: C, 83.2; H, 12.2. Calcd. for $C_{21}H_{42}N_2$: C, 78.3; H, 13.0. Found: (H. H. S.) C, 83.6, 82.8; H, 13.0, 12.9; (Schiff), C, 78.17; H, 13.13.

Attempts to oxidize the high-boiling fraction from heptaldehyde to a pyridine tricarboxylic acid with potassium permanganate gave negative results. As this com-

[15] Lipp, *Ann.*, **205**, 4 (1880).

pound is extremely hard to oxidize, the pyridinecarboxylic acid may have been destroyed during the oxidation.

The writer is indebted to Dr. E. C. Franklin for many helpful suggestions.

## Summary

Evidence is presented to support the postulation that aliphatic imines, hydramides and Schiff's bases are ammono aldehydes. Aside from the known reactions which support this view, it is shown that (1) reactions which should lead to the formation of methylene imine (ammono formaldehyde) yield only hexamethylenetetramine (polymerized ammono formaldehyde), (2) anhydroformaldehydeaniline (ammono formaldehyde-acetal) is ammonolyzed to hexamethylenetetramine and aniline, (3) ethylidene imine (ammono acetaldehyde) is nitridized to acetamidine (ammono acetic acid), (4) ethylidene imine reacts with malonic acid and hydrazine derivatives just as aquo aldehydes do. The formation of pyridine derivatives from aldehydes and ammonia has been shown to be dependent upon the formation of aquo ammono aldols.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE SCHOOL OF MEDICINE, JOHNS HOPKINS UNIVERSITY]

# STUDIES ON OXIDATION-REDUCTION. XVII[1] NEUTRAL RED

BY W. MANSFIELD CLARK AND MARIE E. PERKINS

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Neutral red,[2] named *Toluylenroth* by its discoverer, Witt,[3] has become the best known of those azine dyes called eurhodines. Early in its history it was recognized as a valuable histological and vital stain; and, as has often happened when a dye is constantly available for such purposes, its several properties have been adapted to other biochemical applications. As an acid–base indicator neutral red is used in a range of $P_H$ important biologically. As a reducible dye it has been employed by the bacteriologist and in a manner which will have a particular interest when we shall have described the characteristics of the oxidation–reduction system.

For the moment we are concerned with neutral red exclusively as an

[1] Previous papers of this series have been published in *Public Health Reports* and *Supplements to Public Health Reports*, 1921–1931. The first ten articles have been republished as *Hygienic Laboratory Bulletin*, No. 151, United States Public Health Service. (Manuscript first received July 17, 1931.)

[2] Neutral red is dye No. 825 in Rowe's "Colour Index."

[3] Witt, *Ber.*, **12**, 931 (1879).

oxidation–reduction indicator. Since the compound is similar structurally to useful indicators such as methylene blue, it might be assumed to be a reversible, reliable indicator. Indeed the reductant has been described by several authors as a derivative of dihydrophenazine, as analogous to leuco methylene blue and as a compound which can be oxidized readily to the dye.

Positive evidence in favor of the supposition that neutral red will form a reversible oxidation–reduction system may be inferred from preliminary potentiometric measurements mentioned by Clark and Zoller[4] and from charts of such measurements published without details by Rapkine, Struyk and Wurmser[5] and by Vellinger.[6]

Preliminary explorations by Clark and Zoller had shown that oxidation–reduction systems formed among the azine dyes have characteristic potentials which are much more negative than those of the systems described in previous papers of this series. In addition to its intrinsic interest, this fact seemed to provide a readily available means of extending the series of well-characterized, oxidation–reduction indicators and of providing reagents to test several matters of biochemical importance. Subsequent investigations have proved the advisability of proceeding cautiously with the azines.

In particular it should be emphasized that while the neutral red system does behave in part as a reversible system it also exhibits a peculiar, secondary change. This takes place rapidly within a range of $P_H$ which is of importance biologically. It makes difficult the measurement of reliable potentials and it sets limits to the usefulness of neutral red as an oxidation–reduction indicator.

The following summary of one of many experiments will indicate certain limitations under which potentiometric measurements must proceed.

Rapid reduction of dilute, buffered solutions of neutral red results in almost colorless solutions. If such solutions are immediately removed from a hydrogen or a nitrogen atmosphere and exposed to air, they will be reoxidized. After reoxidation and suitable adjustments of $P_H$ and of dilution, such solutions are found to match the untreated sample within the limitations of an ordinary colorimeter. However, it is significant that after the slow oxidation by air a solution reduced at $P_H$ 5.3 has a noticeable yellow tint.

If, instead of reoxidation immediately after reduction, the solutions are allowed to stand under hydrogen or nitrogen, a very different picture results. At $P_H$ 8.2 the reduced solution remains colorless for an hour at least. At $P_H$ 2.7 the solution slowly acquires a yellow color with green

[4] Clark and Zoller, *Science*, **54**, 557 (1921).

[5] Rapkine, Struyk and Wurmser, *J. chim. phys.*, **26**, 340 (1929).

[6] Vellinger, *Arch. phys. biol.*, **7**, 113 (1929).

fluorescence. At $P_H$ 5.3 the yellow-green fluorescence develops very rapidly.

On reoxidation and adjustment to a common $P_H$ number the solutions which had been held at the more acid and the more alkaline reactions are found to have regained nearly, but not exactly, the color of the original solution. The solution which had been held at $P_H$ 5.3 is found to retain its fluorescence for days, if not made too acid.

What has been said of the attack by oxygen is more or less true of the attack by other oxidizing agents.

While we have made no quantitative comparison between the rate of development of the fluorescence and the rate of change of potential, we feel safe in stating that the rapidity and the extent of drifts in the potentials during titration are roughly correlated with the formation of the material giving the green fluorescence. This material has been isolated in crystalline form and is described in a section of this paper. It will be called the fluorescent material. *Tentatively* we shall now assume that its formation is an irreversible process interfering with accurate potentiometric characterization of a reversible process. Accordingly we shall rule out of immediate consideration a number of experiments in which titrations were made with solutions reduced by prolonged action of hydrogen and a platinum catalyst or in which solutions were reduced by any other means and held in stock for any considerable period. We shall now confine attention to comparatively rapid titrations of neutral red with a reducing agent.

In their preliminary study of the system Clark and Zoller titrated neutral red with titanium trichloride. This reagent has the advantages that it is of sufficient reducing intensity and that it establishes an equilibrium mixture of the dye's reductant and oxidant with the required rapidity. However, the reagent was abandoned in later work because the stock must be preserved in solutions of high acidity. During a titration this acid makes changes in the buffer system which are too large to be subjected to simple and certain correction. We have now used a solution of chromous acetate. With this reagent titration of neutral red in tenth normal hydrochloric acid is unsatisfactory because of the slowness with which potentials become steady. In acid phosphate and acid citrate solutions adjustment is rapid and, although considerable fluorescence develops before the completion of a titration made with careful readings, the results appear to be satisfactory. In alkaline solution the electrode exhibits very steady potentials. Within an intermediate zone, centered near $P_H$ 5 or 6, potentials become erratic and an approach to satisfactory data is attained only by rapid titration.

The solution of chromous acetate was prepared as follows. Hydrous chromic chloride in hydrochloric acid solution was reduced by zinc. From

the filtered solution chromous acetate was precipitated by the addition of sodium acetate. The red, solid chromous acetate was washed repeatedly with water and then transferred to a large volume of deaerated water. Because of the extreme sensitiveness of the chromous acetate to oxygen, all operations were carried out in an apparatus very thoroughly flushed with carbon dioxide. The final solution was washed with and preserved under hydrogen.

Frequent estimates of the normality of the solution over a period of several months showed that it remained at 0.0037 *N*. Since this was somewhat higher than required, the solution was diluted as needed. Variation in the quantities required in titrations of the same amount of dye, as noted in the tables, is due to the use of appreciably different dilutions.

Details of titrations in each of three zones of $P_H$ are summarized in Tables I, II and III.

The methods employed have been described in previous papers of this series. Titrations were made in a shaded room or by dim lamplight. The $P_H$ numbers were determined by careful hydrogen electrode measurements of properly diluted buffer solutions (see tables). By the same means estimates were made of the corrections to apply to the potentials on account of changes in the buffer system during titration. Because of dependence upon the hydrogen electrode measurements, no care was taken to have the stock component solutions of the buffers of *exactly* the composition indicated. Liquid junctions in all cases were made with saturated potassium

TABLE I

TITRATION OF NEUTRAL RED IODIDE WITH CHROMOUS ACETATE

30°C. $P_H$ = 2.156. Approximate composition of buffer: 100 ml. *M* $KH_2PO_4$ + 100 ml. *M* HCl; diluted to 1 liter. Solution titrated: 75 ml. buffer + 5 ml. 0.0005 *M* neutral red. Reference $P_H$ (that of 75 ml. buffer + 5 ml. water) 2.156.

| *y*, ml. | *y-d*, ml. | Reduction, % | $\frac{0.03006}{n}\log [S_R]/[S_0]$, volt | $E_h$ corr., volt | $E_0'$ | Dev. from 0.0461 volt |
|---|---|---|---|---|---|---|
| 1 | 0.15 | 1.24 | −0.0566 | 0.1027 | 0.0461 | 0.0000 |
| 1.5 | 0.65 | 5.56 | − .0370 | .0831 | .0461 | .0000 |
| 2 | 1.15 | 9.88 | − .0289 | .0751 | .0462 | + .0001 |
| 3 | 2.15 | 18.47 | − .0194 | .0655 | .0461 | .0000 |
| 4 | 3.15 | 27.06 | − .0129 | .0590 | .0461 | .0000 |
| 5 | 4.15 | 35.65 | − .0077 | .0540 | .0463 | + .0002 |
| 6 | 5.15 | 44.24 | − .0030 | .0491 | .0461 | .0000 |
| 7 | 6.15 | 52.84 | + .0015 | .0448 | .0463 | + .0002 |
| 8 | 7.15 | 61.43 | .0061 | .0400 | .0461 | .0000 |
| 9 | 8.15 | 70.02 | .0111 | .0343 | ( .0454) | (− .0007) |
| 10 | 9.15 | 78.61 | .0170 | .0258 | ( .0428) | (− .0033) |
| 11 | 10.15 | 87.20 | .0251 | .0108 | ( .0359) | (− .0102) |
| | 11.64 | 100 | .... | .... | .... | .... |
| | | | | Best value | .0461 | |
| | | | | By R. and B. method | .0462 | |

TABLE II

TITRATION OF NEUTRAL RED IODIDE WITH CHROMOUS ACETATE

30° C. $P_H$ = 4.978. Approximate composition of buffer; 100 ml. *M* Na Acetate + 30 ml. *M* HCl; diluted to 1 liter. Solution titrated: 75 ml. buffer + 5 ml. 0.0005 *M* neutral red. Reference $P_H$ (that of 75 ml. buffer + 5 ml. water) 4.978.

| *y*, ml. | *y*-*d*, ml. | Reduction % | $\frac{0.03006}{2}$ log $[S_R]/[S_0]$ volt | $E_h$, volt | $E_0'$, volt | Dev. from −0.2024, volt |
|---|---|---|---|---|---|---|
| 0.5 | 0.18 | 2.95 | −0.0456 | −0.1538 | (−0.1994) | (+0.0030) |
| 1.0 | 0.68 | 11.15 | − .0271 | − .1751 | − .2022 | + .0002 |
| 1.5 | 1.18 | 19.34 | − .0186 | − .1840 | − .2026 | − .0002 |
| 2.0 | 1.68 | 27.54 | − .0126 | − .1899 | − .2025 | − .0001 |
| 2.5 | 2.18 | 35.74 | − .0077 | − .1949 | − .2026 | − .0002 |
| 3.0 | 2.68 | 43.93 | − .0032 | − .1992 | − .2024 | .0000 |
| 3.5 | 3.18 | 52.13 | + .0011 | − .2033 | − .2022 | + .0002 |
| 4.0 | 3.68 | 60.33 | .0055 | − .2077 | − .2022 | + .0002 |
| 4.5 | 4.18 | 68.52 | .0102 | − .2125 | − .2023 | + .0001 |
| 5.0 | 4.68 | 76.72 | .0156 | − .2185 | (− .2029) | (− .0005) |
| 5.5 | 5.18 | 84.92 | .0226 | − .2273 | (− .2047) | (− .0023) |
| | 6.10 | 100 | .... | .... | .... | .... |
| | | | | Average | − .2024 | |
| | | | | By R. and B. method | − .2022 | |

TABLE III

TITRATION OF NEUTRAL RED IODIDE WITH CHROMOUS ACETATE

30° C. $P_H$ = 8.596. Approximate composition of buffer: 500 ml. 0.2 *M* $H_3BO_3$, 30 ml. *M* NaOH, 70 ml. KCl, diluted to 1 liter. Solution titrated: 75 ml. buffer + 5 ml. 0.0005 *M* neutral red. Reference $P_H$ (that of 75 ml. buffer + 5 ml. water) 8.596.

| *y*, ml. | *y*-*d*, ml. | Reduction, % | $\frac{0.03006}{2}$ log $[S_R]/[S_0]$, volt | $E_h$ corr., volt | $E_0'$, volt | Dev. from 0.4149 volt |
|---|---|---|---|---|---|---|
| 1 | 0.45 | 5.84 | −0.0363 | −0.3778 | (−0.4141) | (+0.0008) |
| 2 | 1.45 | 18.83 | − .0191 | − .3958 | − .4149 | .0000 |
| 3 | 2.45 | 31.82 | − .0100 | − .4050 | − .4150 | − .0001 |
| 4 | 3.45 | 44.81 | − .0027 | − .4123 | − .4150 | − .0001 |
| 5 | 4.45 | 57.79 | + .0041 | − .4189 | − .4148 | + .0001 |
| 6 | 5.45 | 70.78 | .0116 | − .4264 | − .4148 | + .0001 |
| 7 | 6.45 | 83.77 | .0214 | − .4358 | (− .4144) | (+ .0005) |
| 8 | 7.45 | 96.75 | .0443 | − .4440 | (− .3997) | (+ .0152) |
| | 7.70 | 100 | .... | .... | .... | .... |
| | | | | Average | − .4149 | |
| | | | | By R. and B. method | − .4150 | |

chloride solution and in essentially the same manner. All titrations were made with solutions deaerated by means of nitrogen.

In Table IV are summarized the values of $E_0'$ [7] obtained by individual titrations in buffered solutions having $P_H$ values of sufficient range to characterize the several values of the slope, $\Delta E_0'/\Delta P_H$. The curve relating $E_0'$ to $P_H$ is shown in Fig. 1, where the data of Table IV are indicated by

[7] $E_0'$ indicates the potential of the system at a specified value of $P_H$ when the ratio of total reductant to total oxidant is unity.

TABLE IV

NEUTRAL RED IODIDE. RELATION OF $E'_0$ TO $P_H$

Determined by separate titrations with chromous acetate. Values used in calculations: $K_0 = 1.59 \times 10^{-7}$; $K_{r1} = 6.92 \times 10^{-7}$; $K_{r2} = 5.01 \times 10^{-6}$; $E_0 = 0.240$. $E'_0 = E_0 - 0.03006 \log [[H^+] + K_0] + 0.03006 \log [[H^+]^2 + K_{r2}[H^+] + K_{r1}K_{r2}] - 0.0601\ P_H$.

| Buffer | $P_H$ | $E'_0$ found, volt | $E'_0$ calcd., volt | Found − calcd. |
|---|---|---|---|---|
| Phosphate | 2.156 | +0.046 | +0.046 | 0.000 |
| Citrate | 2.753 | − .009 | − .008 | − .001 |
| Citrate | 3.495 | − .075 | − .075 | .000 |
| Acetate | 4.640 | − .176 | − .176 | .000 |
| Acetate | 4.978 | − .202 | − .204 | + .002 |
| Citrate | 5.756 | − .259 | − .259 | .000 |
| Phosphate | 6.080 | − .280 | − .278 | − .002 |
| Phosphate | 6.488 | − .295 | − .299 | + .004 |
| Phosphate | 7.105 | − .330 | − .331 | + .001 |
| Borate | 8.163 | − .391 | − .391 | .000 |
| Borate | 8.596 | − .415 | − .417 | + .002 |

the centers of the open circles. The trends of the curve were roughly confirmed by use of a solution of neutral red partly reduced in *acid* solution and introduced into various buffer solutions. The measurements with this preformed mixture were extended to $P_H$ 12 and indicated that the slope ($\Delta E'_0/\Delta P_H = -0.0601$), characteristic at high values of $P_H$, continues this far into the region of alkalinity. Also supplementary data were obtained by rapid titrations which included only four or five increments of reducing agent. The latter data were analyzed by the method presently to be described. The resulting values of $E'_0$ are indicated in Fig. 1 by the centers of blacked circles.

Figure 1 seems to be in substantial agreement with the less detailed figure for the neutral red system pub-

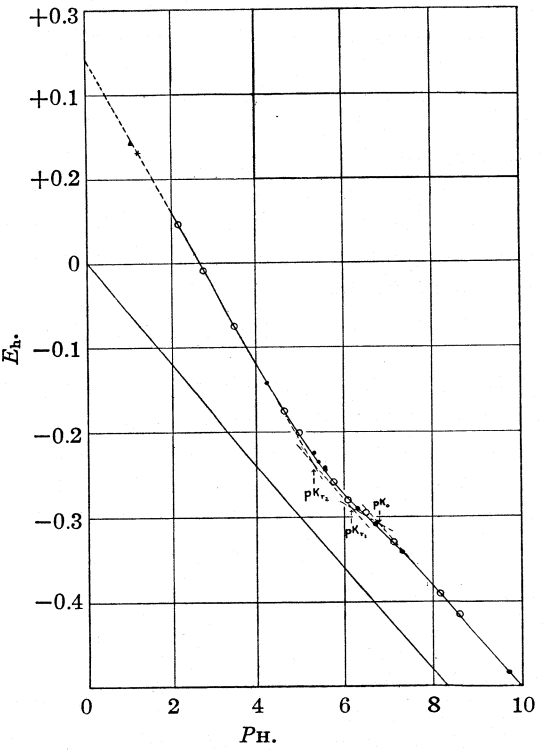



Fig. 1.—Neutral red, relation of $E'_0$ to $P_H$.

lished by Vellinger.[6] It is important to note that Vellinger made his titrations with $Na_2S_2O_4$. Unfortunately neither Vellinger nor Rapkine, Struyk and Wurmser,[5] who record only a few points on the curve, give adequate details.

In each of our titrations it was found that considerable reducing agent was used before the titration curve began to flatten. Experience has revealed cases where this may be attributed to an oxidizing impurity in the sample of dye. In the present instance we are loath to assume this because we used a beautiful preparation of neutral red iodide made by Phillips and Cohen.[8] Indeed the calculated excesses of reducing agent varied sufficiently in titrations of the same amount of dye to indicate that an impurity of the dye was not entirely responsible. Doubtless the buffer solutions contained traces of reducible material. However, we were unable definitely to prove this by blank titrations with chromous acetate because with this reagent, in the absence of a definitely reversible system, potentials are indefinite.

Thus there was no definite origin of a titration curve. To make matters worse there was no certain end-point. In most instances it was quite evident that the "irreversible" process became so rapid near the end of a titration that the end-point was obscured. Having no reliable origin and end-point we were forced to depend upon the intermediate data in calculating the characteristics of each curve. This can be done by the method of Reed and Berkson.[9]

Since we have made changes in their symbols appropriate to the case at hand and since the method deserves some emphasis, the equations will be stated. Assume that the titration is made at constant $P_H$ or that the data have been properly corrected to meet this condition. Then equation (1) will be applicable

$$E_h = E_0' + 0.03006 \log \frac{A - (y - d)}{y - d} \qquad (1)$$

$y$ is the number of milliliters of reducing agent actually used in reaching the state where the potential is $E_h$; $d$ is the extra number of milliliters of reducing agent consumed before the dye is attacked; $A$ is the number of milliliters required for 100% reduction of the dye (see figure 2A).

Make an arbitrary shift of the origin of potential so that

$$E_h + E_n = E \qquad (2)$$

where $E = 0$ when $y = y_n$. Let

$$E_0' + E_n = - 0.03006 \log C \qquad (3)$$

and let

$$E/0.03006 = p$$

[8] Phillips and Cohen, *Stain Technology*, **2**, 74 (1927).

[9] Reed and Berkson, *J. Phys. Chem.*, **33**, 760 (1929).

With these definitions the development by Reed and Berkson may be followed to equation (4)

$$y = (1 + C)\frac{y_n - y10^p}{1 - 10^p} - dC \qquad (4)$$

Or if $(y_n - y10^p)/(1 - 10^p) = x$

$$y = (1 + C)x - dC \qquad (5)$$

Also

$$A = (y_n - d)(1 + C) \qquad (6)$$

Equation 5 is the equation of a straight line which cuts the $y$ axis at $-d$ and which has the slope $(1 + C)$. See an experimental case in Fig. 2B. Therefore, if the data conform closely to equation (1), it is possible to draw a "best" straight line through the loci $x$, $y$, and to estimate $d$ and $C$ of equation (5). Then $A$ is calculated with equation (6) or $E'_0$ is calculated with equation (3).

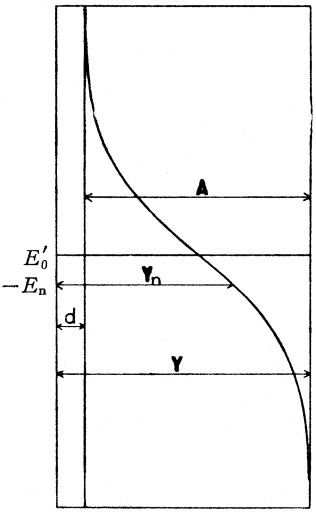



Fig. 2A.

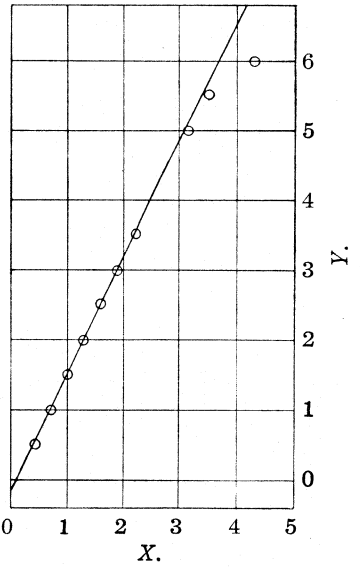



Fig. 2B.

The method places a rather heavy burden upon the accuracy of the arbitrarily selected reference point and upon the judgment with which the "best" straight line is placed. Therefore, and instead of repeating the calculations with several reference points, we have felt justified in making slight shifts[10] in the preliminary values of $A$ and $d$ in order to eliminate from tables such as I the more obviously erroneous trend in a series of values of $E'_0$ which usually remained after the first estimate.

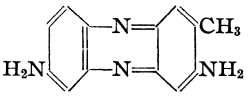
[10] With one exception, such shifts involved differences of less than 0.5 millivolt between a value of $E'_0$ obtained by one trial of Reed and Berkson's method and the value finally accepted. The average difference was 0.3 millivolt.

In Fig. 2B there is plainly evident, in a specific instance, the departure of the experimental points where the end-point is approached. Similar discrepancies are shown in another way by Tables I, II and III where the values of $E_0'$ are shown to vary as the end-point is approached.

Better data with regard to end-point, origin, or $E_0'$ were not obtained by using a carefully crystallized preparation of neutral red base.

For purposes of comparison, measurements were made with "simple neutral red" and with dimethylaminomethylphenazine.

**Simple Neutral Red.**—No improvement in origin of titration curves, a slight improvement in end-point and a considerable improvement in the stability of potentials were obtained with "simple neutral red iodide." This compound is called "simple neutral red iodide" because Bernthsen and Schweitzer[11] called the base (formula I) "das einfachste Toluylenroth."




(I)

We used material prepared by Dr. Phillips in accordance with the directions of Bernthsen and Schweitzer and converted to the iodide by the procedure used in preparing neutral red iodide. We find the nitrogen to be 15.9 and 15.8%. The theoretical for $C_{13}H_{13}N_4I$ is 15.9.

A fluorescent material forms in the reduced solutions.

Tables V, VI and VII give the details of titrations within the three

TABLE V

TITRATION OF "SIMPLE NEUTRAL RED" WITH CHROMOUS ACETATE

30°C. $P_H$ = 3.454. Approximate composition of buffer: 100 ml. 1 *M* citric acid +85 ml. 1 *M* NaOH, diluted to 1 liter. Solution titrated: 75 ml. buffer +5 ml. 0.0005 *M* simple neutral red. Reference $P_H$ (that of 75 ml. buffer +5 ml. water) 3.454.

| *y*, ml. | *y* − *d*, ml. | Reduction, % | $\frac{0.03006}{2}$ log $[S_R]/[S_0]$, volt | $E_h$ corr., volt | $E_0'$ | Dev. from −0.0728 volt |
|---|---|---|---|---|---|---|
| 1.2 | 0.3 | 5.60 | −0.0369 | −0.0360 | −0.0729 | −0.0001 |
| 1.6 | 0.7 | 13.06 | − .0247 | − .0480 | − .0727 | + .0001 |
| 2.0 | 1.1 | 20.52 | − .0177 | − .0551 | − .0728 | .0000 |
| 2.5 | 1.6 | 29.85 | − .0112 | − .0617 | − .0729 | − .0001 |
| 3.0 | 2.1 | 39.18 | − .0057 | − .0671 | − .0728 | .0000 |
| 3.5 | 2.6 | 48.51 | − .0008 | − .0721 | − .0729 | − .0001 |
| 4.0 | 3.1 | 57.84 | + .0041 | − .0769 | − .0728 | .0000 |
| 4.5 | 3.6 | 67.16 | .0093 | − .0821 | − .0728 | .0000 |
| 5.0 | 4.1 | 76.49 | .0154 | − .0883 | − .0729 | − .0001 |
| 5.5 | 4.6 | 85.82 | .0235 | − .0967 | − .0732 | − .0004 |
| 6.0 | 5.1 | 95.15 | .0389 | − .1115 | − .0726 | + .0002 |
| | 5.36 | 100 | | | | |
| | | | Average | | −0.0728 | |
| | | | By R. and B. method | | − .0730 | |

[11] Bernthsen and Schweitzer, *Ann.*, **236**, 332 (1886).

TABLE VI

TITRATION OF "SIMPLE NEUTRAL RED" WITH CHROMOUS ACETATE

30°C. $P_H$ = 6.08. Approximate composition of buffer: 100 ml. 1 $M$ $KH_2PO_4$ +17 ml. 1 $M$ NaOH; diluted to 1 liter. Solution titrated: 75 ml. buffer +5 ml. 0.0005 $M$ simple neutral red. Reference $P_H$ (that of 75 ml. buffer +5 ml. water) 6.080.

| $y$, ml. | $y-d$, ml. | Reduction, % | 0.03006 log $[S_R]/[S_0]$, volt | $E_h$ corr., volt | $E_0'$ | Dev. from −0.2704 volt |
|---|---|---|---|---|---|---|
| 1.0 | 0.05 | 0.82 | −0.0626 | −0.2185 | (−0.2811) | −0.0107 |
| 1.5 | 0.55 | 9.02 | − .0302 | − .2403 | − .2705 | − .0001 |
| 2.0 | 1.05 | 17.21 | − .0205 | − .2498 | − .2703 | + .0001 |
| 2.5 | 1.55 | 25.41 | − .0141 | − .2564 | − .2705 | − .0001 |
| 3.0 | 2.05 | 33.61 | − .0089 | − .2616 | − .2705 | − .0001 |
| 3.5 | 2.55 | 41.80 | − .0043 | − .2661 | − .2704 | .0000 |
| 4.0 | 3.05 | 50.00 | .0000 | − .2704 | − .2704 | .0000 |
| 4.5 | 3.55 | 58.20 | + .0043 | − .2746 | − .2703 | + .0001 |
| 5.0 | 4.05 | 66.39 | .0089 | − .2793 | − .2704 | .0000 |
| 5.5 | 4.55 | 74.59 | .0141 | − .2845 | − .2704 | .0000 |
| 6.0 | 5.05 | 82.79 | .0205 | − .2914 | (− .2709) | − .0005 |
| 6.5 | 5.55 | 90.98 | .0302 | − .3024 | (− .2722) | − .0018 |
| 7.0 | 6.05 | 99.18 | .0626 | − .3164 | (− .2538) | + .0166 |
| | 6.10 | 100.00 | | | | |
| | | | Average | | −0.2704 | |
| | | | By R. and B. method | | − .2705 | |

TABLE VII

TITRATION OF "SIMPLE NEUTRAL RED" WITH CHROMOUS ACETATE

30°C. $P_H$ = 8.591. Approximate composition of buffer: 500 ml. 0.2 $M$ $H_3BO_3$ +30 ml. $M$ NaOH +70 ml. $M$ KCl; diluted to 1 liter. Solution titrated: 75 ml. buffer +5 ml. 0.0005 $M$ simple neutral red. Reference $P_H$ (that of 75 ml. buffer +5 ml. water) 8.591.

| $y$, ml. | $y-d$, ml. | Reduction, % | 0.03006 log $[S_R]/[S_0]$, volt | $E_h$ corr., volt | $E_0'$ | Dev. from −0.4168 |
|---|---|---|---|---|---|---|
| 1.0 | 0.2 | 3.64 | −0.0428 | −0.3733 | (−0.4161) | +0.0007 |
| 1.5 | 0.7 | 12.73 | − .0251 | − .3913 | − .4164 | + .0004 |
| 2.0 | 1.2 | 21.82 | − .0167 | − .4000 | − .4167 | + .0001 |
| 2.5 | 1.7 | 30.91 | − .0105 | − .4063 | − .4168 | .0000 |
| 3.0 | 2.2 | 40.00 | − .0053 | − .4115 | − .4168 | .0000 |
| 3.5 | 2.7 | 49.09 | − .0005 | − .4164 | − .4169 | − .0001 |
| 4.0 | 3.2 | 58.18 | + .0043 | − .4212 | − .4169 | − .0001 |
| 4.5 | 3.7 | 67.27 | .0094 | − .4262 | − .4168 | .0000 |
| 5.0 | 4.2 | 76.36 | .0153 | − .4321 | − .4168 | .0000 |
| 5.5 | 4.7 | 85.45 | .0231 | − .4396 | − .4165 | + .0003 |
| 6.0 | 5.2 | 94.55 | .0373 | − .4528 | (− .4155) | + .0013 |
| | 5.5 | 100.00 | | | | |
| | | | "Best value" | | −0.4168 | |
| | | | By R. and B. method | | − .4172 | |

distinctive regions of $P_H$ and Table VIII summarizes the data for several values of $P_H$. The $E_0'$:$P_H$ curve lies so close to that of neutral red that it has been omitted from Fig. 1 to avoid confusion. $E_0$ is 0.237. $E_0$ for neutral red is 0.240.

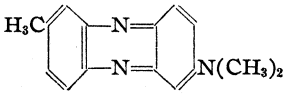
TABLE VIII

SIMPLE NEUTRAL RED. RELATION OF $E_0'$ TO $P_H$

Determined by separate titrations with chromous acetate. Values used in calculations: $K_0 = 4.79 \times 10^{-7}$; $K_{r1} = 1.10 \times 10^{-6}$; $K_{r2} = 1.12 \times 10^{-5}$. $E_0 = 0.237$. $E_0' = E_0 - 0.03006 \log [[H^+] + K_0] + 0.03006 \log [[H^+]^2 + K_{r2}[H^+] + K_{r1}K_{r2}] - 0.0601\ P_H$.

| Buffer | $P_H$ | $E_0'$ found | $E_0'$ calcd. | Found − calcd. |
|---|---|---|---|---|
| Phosphate | 2.127 | +0.045 | +0.045 | 0.000 |
| Citrate | 2.744 | − .013 | − .010 | − .003 |
| Citrate | 3.454 | − .073 | − .074 | + .001 |
| Acetate | 4.624 | − .176 | − .175 | − .001 |
| Acetate | 4.978 | − .204 | − .202 | − .002 |
| Citrate | 5.242 | − .218 | − .221 | + .003 |
| Citrate | 5.750 | − .252 | − .253 | + .001 |
| Phosphate | 6.080 | − .270 | − .272 | + .002 |
| Phosphate | 6.487 | − .293 | − .294 | + .001 |
| Phosphate | 7.468 | − .350 | − .350 | .000 |
| Borate | 8.160 | − .392 | − .391 | − .001 |
| Borate | 8.591 | − .417 | − .417 | .000 |
| Phosphate | 10.95 | − .557 | − .559 | + .002 |

**Dimethylaminomethylphenazine** of formula II was prepared by Dr. Max Phillips from commercial neutral red chloride




(II)

in accordance with the method of Bernthsen and Schweitzer.[11] The material was crystallized first from dilute ethanol and was recrystallized once from "gasoline" and finally from benzene. The melting point of the glistening red needles agreed with that given by Bernthsen and Schweitzer. A fluorescence develops in the reduced solutions.

The components of the system have such low solubilities that it can be conveniently studied only in solutions of $P_H$ number less than 5, where the salts form. However, the relation of $E_0'$ to $P_H$ in acid solutions has a theoretical interest. The system lacks the amino group found in neutral red. Consequently the reductant does not form a bivalent cation in mildly acid solution and the curve, instead of inflecting to the slope $\Delta E/\Delta P_H = -0.09$, as in the other cases, maintains the slope $\Delta E/\Delta P_H = -0.06$.

While our data are not accurate enough to demonstrate this thoroughly, we support this conclusion as follows. Portions of a mixture of oxidant and reductant, prepared by partial reduction of a slightly acidified solution of the oxidant, were introduced into a series of buffers. The potentials drifted somewhat but fell near a straight line of the specified slope. Data for neutral and alkaline solutions, where precipitates occurred, were neglected.

Independent titrations of the oxidant with chromous acetate gave appreciably varying values of $E_0'$ depending upon the rapidity of operation. We judged $E_0'$ at $P_H$ 2.92 to be +0.031 and at $P_H$ 3.50 to be −0.001. The difference is 0.032 volt against the theoretical value of 0.035, if $\Delta E_0'/\Delta P_H = -0.0601$. $E_0$ estimated from these titrations would average 0.208. Obviously there would be no object in a comparison[12] between this $E_0$ and that of neutral red.

**Equations.**—The data for neutral red and simple neutral red conform to equation (7). This was derived in more comprehensive form by the scheme outlined in the second paper[13] of this series and then simplified by the elimination of dissociation constants which are without significance in the range of $P_H$ employed.

$$E_h = E_0 - 0.03006 \log \frac{[S_R]}{[S_0]} - 0.03006 \log \frac{K_0 + [H^+]}{K_{r1}K_{r2} + K_{r2}[H^+] + [H^+]^2} + 0.03006 \log [H^+]^2 \quad (7)$$

$E_h$ is the observed potential at 30°, referred to the "normal hydrogen electrode." $E_0$, the "normal potential," is the potential at unit concentration of all represented components. $[S_R]$ is the molar concentration of total reductant. $[S_0]$ is the molar concentration of total oxidant. $[H^+]$ is the hydrion concentration, assumed for the present purposes to be calculable from the $P_H$ numbers.[14]

$$K_0 = \frac{[Ox][H^+]}{[OxH^+]} \quad (8)$$

$$K_{r1} = \frac{[H_2\ Red][H^+]}{[H_3\ Red^+]} \quad (9)$$

$$K_{r2} = \frac{[H_3\ Red^+][H^+]}{[H_4\ Red^{++}]} \quad (10)$$

$K_0$ for neutral red is assumed to be $1.59 \times 10^{-7}$, corresponding to $pK_0 = 6.80$. Kolthoff[15] gives $pK_0 = 6.85$. For simple neutral red $pK_0 = 6.3$. This was determined roughly by the usual colorimetric method at half-transformation. Both of these constants are approximate only. Indeed Mr. T. T. Chen, of this Laboratory, has some evidence that the usual relation between $P_H$ and degree of color transformation is not followed exactly by neutral red. Kolthoff's data suggest this. The subject needs investigation.

The $pK$ values corresponding to the constants listed in Tables IV and VIII are

[12] Among organic systems there are many instances in which "normal potentials" are without concrete significance.

[13] See Clark and Cohen, *Public Health Reports*, **38**, 666 (1923).

[14] There were used the conventions proposed by Clark, "The Determination of Hydrogen Ions," 1928, 3d ed., Chapter 23.

[15] Kolthoff, *Rec. trav. chim.*, [4] **5**, 144 (1924).

| | | | |
|---|---|---|---|
| Neutral red: | $pK_0 = 6.80$ | $pK_{r1} = 6.16$ | $pK_{r2} = 5.30$ |
| Simple neutral red: | $pK_0 = 6.32$ | $pK_{r1} = 5.96$ | $pK_{r2} = 4.95$ |

**The Fluorescent Material.**—The fluorescent material has attracted the attention of bacteriologists but, so far as we know, it has not been adequately studied by organic chemists. Rothberger[16] noted that it forms in cultures of *B. coli* more readily than in cultures of *Bact. typhosum*. Although this helpful diagnostic use of neutral red media was found not to be specific, it stimulated many investigations which may be traced through references given by Guerbet,[17] by Geilinger and Schweizer[18] and by Chamot and Sherwood.[19]

From time to time one investigator or another confused the processes leading to the several colors which are produced by various combinations and degrees of acidity, reduction and the change to the fluorescent material. Now that somewhat clearer distinctions are made possible by the methods in use, one can piece together citations from the literature to make a coherent description covering several of our own observations. A review is omitted because of the lengthy qualifications of previous views which would have to be introduced. Suffice it to say that no longer should there be confusion between the yellow oxidant in alkaline solution and the yellow material formed upon reduction. Also it seems evident to us that the yellow fluorescent material formed in reduced solutions of neutral red is distinct from the initial product of reduction and that its formation depends upon the $P_H$ number of the solution. Failure to recognize this has been one of the main sources of confusion.

Preparation of the material in crystalline form was accomplished as follows. Having observed that the fluorescent material may form subsequent to reduction of neutral red by two equivalents of a reducing agent and that it forms readily in the range $P_H$ 4 to 6, we reduced the solution of neutral red while it was buffered heavily in this region. Sodium dithionite ($Na_2S_2O_4$), in excess, was used as the reducing agent. The solution was allowed to stand overnight in order that the conversion to the fluorescent material should be complete.

The fluorescent material precipitates and slowly becomes appreciably crystalline when the solution is made alkaline; but, unlike the crystals of leuco neutral red, those of the fluorescent material may be filtered and washed with water in the presence of air without oxidation being apparent to superficial observations.

After extensive washing with water the material was dissolved in ethanol, filtered and precipitated in crystal form by addition of water.

[16] Rothberger, *Centr. Bakt. Parasitenk.*, 1 Abt., **24,** 513 (1898); **25,** 15, 69 (1899).
[17] Guerbet, "Thèse," University of Paris, 1911.
[18] Geilinger and Schweizer, *Biochem. Z.*, **138,** 72, 92 (1923).
[19] Chamot and Sherwood, THIS JOURNAL, **39,** 1755 **(1917).**

In preparing sample 8 an acetate buffer was used when the reduction took place and the sample was finally crystallized a second time from methanol and water.

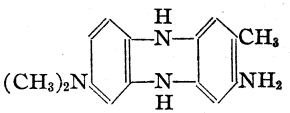
In preparing sample 10 a phosphate buffer was used and the sample was finally crystallized a second and a third time from methanol and water.

The crystals are bars, frequently elongated as "needles," and appear to be orthorhombic. When first isolated these pale yellow crystals have sharp edges and clean surfaces. Placed between crossed nicols, they exhibit their anisotropic nature distinctly. When dried the crystals appear to be checkered. Then, between crossed nicols, they transmit some light at all horizontal orientations of the microscope slide upon which they lie. It is as if the checkered appearance represented a breaking of the crystal with more or less random orientation of parts, the parts preserving the outline of the original unit. Recrystallization of such checkered or crazed crystals yields abundantly the original clean crystals.

Concentrated solutions in alcohols have a color and fluorescence which remind one of a fluorescent machine oil. On dilution the fluorescence becomes brilliant. The material is slightly soluble in water and exhibits a fluorescence easily detected at a dilution of one part in 100,000 parts of water.

Since dithionite was used exclusively as the reducing agent in our preparations it should be mentioned that our first observation of the crystals was in a case where a concentrated solution of neutral red had been reduced by hydrogen and platinum asbestos.

Below are summarized analyses of samples dried over phosphorus pentoxide. For comparison are shown the theoretical values of leuco neutral red on the supposition that it has the structure indicated by formula III.



(III)

| Sample | No. 6 | No. 7 | No. 8 | | No. 10 | | Calcd. for $C_{15}H_{18}N_4$ |
|---|---|---|---|---|---|---|---|
| Carbon | .. | .. | 70.6 | 70.7 | 70.1 | 70.4 | 70.82 |
| Hydrogen | .. | .. | 7.5 | 7.3 | 7.4 | 7.5 | 7.14 |
| Nitrogen | 21.2 | 21.3 | 21.3 | 21.7 | 21.3 | | |
| | | 21.3 | 21.6 | 21.7 | 21.2 | | 22.04 |

Samples 5, 8 and 10 were tested for sulfur and halogens. None was found. The analytical results are sufficiently close to the values for the assumed composition to suggest that the discrepancies are due to some slight impurity. In this connection the following facts should be stated. When dried for analysis the crystals are slightly hygroscopic. They exhibit

the checkered appearance noted above. The alcoholic solution leaves on a filter paper an extremely small trace of dark material.

A molecular weight determination was made with diphenylamine as solvent and a ten-pair, copper–constantan thermoelement for the measurement of freezing point depression. Ortho tolidine was used to determine the cryoscopic constant (8.53°). With an error that may have been as great as ±10% we found the fluorescent material to have an apparent molecular weight of 247; duplicate, 248. The theoretical for formula III is 254. Complete protection against oxygen was not attempted but nitrogen was passed over the solution before and during measurements. No color change indicative of oxidation appeared.

In addition to what has already been stated the following facts confirm the supposition that a distinction may be drawn between the fluorescent material and leuco neutral red.

If "leuco neutral red" be formed in a solution of $P_H$ 8.3, where the dilute solution exhibits no fluorescence, and if it then be transposed to a buffer solution of $P_H$ 5 or 6, it becomes transformed into the fluorescent material. When this is carried back to $P_H$ 8.3 it exhibits fluorescence.

With the aid of the hydrogen electrode we attempted to define the titration curve. For various reasons the results were considered untrustworthy. Titrations with the aid of a glass electrode seemed more reliable and yielded the following important results. There is no evidence of a dissociation exponent corresponding to any $P_H$ number between 2 and 7.5. If 254 be the molecular weight, one equivalent of acid (±5%) is neutralized by a basic group functioning at $P_H$ values greater than 7.5. No accurate evaluation of the dissociation exponent was practicable because of the very low solubility of the free base.

Thus it is evident that the two dissociation exponents of leuco neutral red, which were determined, by the method previously described, to be approximately 6.2 and 5.3, have been altered in the transformation of leuco neutral red to the fluorescent material. If corresponding structural groups remain, the dissociation exponent of the one has certainly been increased and the other has presumably been decreased.

There is a remarkable distinction between the fluorescent material and leuco neutral red in ease of oxidation. The colorless solutions formed upon *rapid* reduction of neutral red oxidize very rapidly when exposed to air. Neutral and alkaline solutions of the fluorescent material become oxidized by air with extreme slowness. This distinction is even more remarkable in the case of the solids. A suspension of neutral red base in borate buffer ($P_H$ = 8.2), protected by a stream of nitrogen, was reduced by sodium dithionite ($Na_2S_2O_4$). Portions of the crystals were withdrawn from time to time, were examined under the microscope and were found to retain their colorless appearance if protected by the reducing mother liquor. As soon

as the mother liquor was drained away superficial oxidation by air was almost instantaneous. Some of the crystals, held under nitrogen, were washed with water containing a little dithionite and quickly transferred to a vacuum desiccator. On the following morning when the dry material was exposed to air the oxidation was so vigorous that there was a large rise of temperature and some smoke. A dry sample of the fluorescent material, prepared in 1927 by Dr. Max Phillips, has not changed its appearance within the ensuing years; nor have any of our own preparations during a period of several months shown any change other than the checkering of the crystals noted above. This is probably not due to an oxidative change.

Except in acid solution, admixture of the fluorescent material with neutral red gives uncertain and drifting potentials as if the two materials are of different systems.

One might infer from these contrasts that leuco neutral red becomes transformed irreversibly into the fluorescent compound. On the other hand, the conduct of the isolated, fluorescent material, when placed in *acid* solution, makes this base appear as an "inactive" form of leuco neutral red, possibly slightly impure.

In tenth normal hydrochloric or sulfuric acid the fluorescent material can be titrated with benzoquinone, bichromate or thallic chloride. The electrode potentials attain apparent equilibrium with great rapidity. They are not easily displaced by polarization and at first they seem remarkably steady. Rapid titrations yield data which conform approximately to a typical titration curve involving two equivalents. However, careful study shows two disturbing effects. First, if the solution has been freshly prepared, it is noticed that, as the titration proceeds with any of the mentioned oxidizing agents, the potentials acquire a tendency to drift to more negative values, especially near the apparent end-point. Such a drift persists for hours. Second, if acid solutions of the fluorescent material are held for long periods previous to titration, the titration curve changes its form. The greater part of its course follows the original but the first part now becomes troublesome. This first section suggests the presence of a new and more *negative* system. With its progressive formation the titer of the solution as a whole falls.

These observations with solutions of the isolated fluorescent material clarify difficulties which were encountered in studying acid solutions of neutral red reduced by hydrogen and platinized asbestos. With the varying times of such reductions, changes were sufficiently variable to preclude reproducible results.

In Fig. 1 at $P_H$ 1.05 there is shown by the center of a triangle the average of two values of $E_0'$ obtained by titrations with benzoquinone of a solution of neutral red after reduction by hydrogen and platinum. In the second titration, made a day after the first, the titer had fallen off 30%.

A bichromate titration of a *freshly* prepared solution of the fluorescent material in oxygen-free, approximately tenth-normal sulfuric acid yielded a value of $E_0'$ which fell upon the projected curve of Fig. 1 as shown by the cross. The titration curve conformed fairly closely to the type for two equivalents. Depending upon the rapidity of titration, slight but appreciable differences in the amounts of total oxidizing agent were found. Judging the situation both from the point of view of the apparent end-points and from the analysis of the curves by the method of Reed and Berkson, we can draw one or another of the following conclusions. (1) The amount of fluorescent material used and the amount of bichromate consumed were such that the molecular weight of the fluorescent material is 270; or (2), if the fluorescent material has the molecular weight 254, that of leuco neutral red, it consumed 94% of the theoretical amount of bichromate; or (3), if the fluorescent base is an inactive form of leuco neutral red, 94% had been made active by the acid.

Adopting the last assumption as a working hypothesis we imagined that decreasing proportions would be titratable if $P_H$ were progressively increased. This was tested as follows.

A weighed portion of the fluorescent material was dissolved in slightly more than two equivalents of acid, assuming a molecular weight of 254. Like portions of this solution were added to buffer solutions and after about a half-hour, when the potentials were fairly steady, each solution was titrated rapidly with thallium chloride. Since titrations were made rapidly in an effort to estimate the amounts of more readily available reductant, the data of Table IX are not very accurate. However, it may be said that in the more acid solutions the titration curves appeared to be typical and that the end-points were reasonably good. At the higher $P_H$ values the potentials were never steady and the amounts of oxidizing agent consumed can only be guessed.

TABLE IX

AMOUNTS OF 0.002 *N* $TlCl_3$ (*A*) REQUIRED TO REACH APPARENT END-POINTS IN RAPID TITRATIONS OF BUFFERED SOLUTIONS CONTAINING 5 ML. OF A SOLUTION MADE WITH 0.0254 G. OF "FLUORESCENT MATERIAL" PER 100 ML.

| $P_H$ | *A*, ml. | Percentage of possibly theoretical value | Percentage calculated assuming 50% at $P_H$ = 2.4 |
|---|---|---|---|
| 1.1 | 4.8 | 96 | 95 |
| 2.2 | 3.1 | 62 | 61 |
| 2.75 | 1.8 | 36 | 31 |
| 4.6 | (0.6) | (1.2) | 0.6 |
| 5.3 | (0.3) | (0.6) | 0.1 |

Table IX reveals that the crude working hypothesis was confirmed as far as it can be by such an experiment. Table IX also develops a relation that is deceptive in so far as it bears a superficial resemblance to a dissociation curve. It is

$$P_H = 2.4\,(?) + \log \frac{1 - A}{A}$$

where $A$ is the fraction of titratable material.

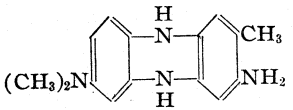
It has already been noted that oxidation of a *freshly* prepared, acid solution of the fluorescent material yields a value of $E_0'$ which is consistent with the supposition that neutral red is the oxidant which is regenerated. This supposition was confirmed as follows. Air oxidation of a *freshly* prepared, acid solution of the fluorescent material yielded a red solution which when diluted to $254 \times 10^{-5}$ g. of fluorescent material per liter, gave a spectrophotometric absorption curve which was identical in contour and in peak with that of a $1 \times 10^{-5}$ molar solution of neutral red iodide. A freshly prepared, acid solution of the fluorescent material was subjected to oxidation by air. From this there precipitated on addition of alkali a color base which, when examined as an acid–base indicator, was found to have a half-transformation point at $P_H$ 6.8. This is the value for neutral red.

## Discussion

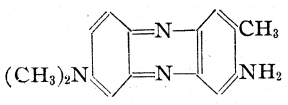
The data reported in the first part of this paper were obtained by avoiding, incompletely but as far as was practicable, the disturbing effects which have been correlated with the formation of the fluorescent material. The data are not all that one would wish them to be as accurately characterizing a reversible oxidation–reduction system; but, if there be a legitimate allowance for the instability of the system, the data are convincing. In particular it may be said that there seems no avoidance of the conclusion that, throughout the range of $P_H$ employed, two paired equivalents are concerned in the reduction. This has an important bearing upon the nature of the reductant. Also the inflections of the $E_0'$:$P_H$ curve are what might reasonably be expected and are comparable with the inflections found in cases for which there are more accurate data.

Since such physical measurements contribute nothing that is compellingly conclusive regarding structure but do contribute suggestions, we shall avoid lengthy comment upon the long-discussed structural problem and shall note the following.

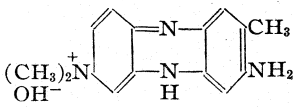
The slope $\Delta E_0'/\Delta P_H$ is $-0.0601$ in the alkaline region. This implies the fixation of two hydrions when the oxidant is converted to the reductant. Therefore, if leuco neutral red, as the free base in alkaline solution, has the structure indicated by formula III




III




IV




V

neutral red in the same range of $P_H$ is represented by formula IV or V. The dissociation of neutral red as a base is 50% at $P_H$ 6.8. Therefore its dimethylamino group (or possibly its amino group) is a very much more weakly basic group than the similarly situated dimethylamino group in certain analogous compounds.[20] Consequently the "orthoquinone" structure IV seems preferable. This would not preclude each of such tautomers as the ions of IV and V from sharing the field in acid solution.

The curve relating $E_0'$ to $P_H$ approaches rather closely the curve of the hydrogen electrode potential (see Fig. 1). Let the difference between $E_0'$ and the potential of the hydrogen electrode under one atmosphere of hydrogen be found by use of equation (7) and the equation for the hydrogen electrode. Let the difference be $E_d$. By the "method of maxima and minima" and use of the constants found in Table IV, $E_d$ is shown to be a minimum at $P_H$ 5.8. At this level $E_d$ is only 0.087 volt and the neutral red system at 99.87% reduction exhibits an electrode potential equal to that of the hydrogen electrode under one atmosphere of hydrogen.

Since the system is distinctly more "negative" than any of the indicator systems described in previous articles of this series, it might appear that it is available for several biochemical applications that await the development of just such a reagent. However, the peculiar secondary change virtually places the system among those which are more or less irreversible. With such systems the interpretation of color change in terms of potential cannot easily be made exact. Therefore the neutral red system can be used as an oxidation–reduction indicator only for rough comparisons. One such instance has a special interest.

It has already been noted that Rothberger[16] found cultures of *B. coli* (*Escherichia coli*) to reduce neutral red with consequent fluorescence, while he found that cultures of *Bact. typhosum* do not reduce this dye. Therefore, it appears that *B. coli* can bring about the more intense reduction.

In 1920 one of us, following the work of Gillespie,[21] compared the potentials of platinum electrodes in cultures of several bacterial species.[22] It was found that while electrodes in cultures of *B. coli* can attain and even pass the potential of a hydrogen electrode under one atmosphere of hydrogen, the electrodes in cultures of *Bact. typhosum* definitely fall short of such values.

The correlation between the differentiation by electrode potentials and the differentiation by neutral red is now obvious. In noting this correlation we are quite appreciative of the limitations in definiteness and

[20] See the comparison between the dissociation constants of toluylene blue, Bindschedler's green, Lauth's violet and methylene blue made by Phillips, Clark and Cohen "Supplement 61" to *Public Health Reports*, 1927, and the resulting argument concerning allocations.

[21] Gillespie, *Soil Science*, 9, 199 (1920).

[22] See also Cannan, Cohen and Clark, "Supplement No. 55," *Public Health Reports*, 1926.

accuracy pertaining to each of the methods. Furthermore we would not imply that the differentiation noted would hold under all cultural conditions. Nevertheless, crude correlations such as this have their place in the accumulating body of evidence that electrode potentials in biological systems have significance.

When the "potentials" of bacterial cultures are better known it will be possible to define more clearly the cases in which neutral red may be used in cultures as an indicator of $P_H$ number and the cases where such use is interfered with by reduction.

Our study of the fluorescent material obviously is incomplete, and cannot define the structure. The accepted formula for leuco neutral red affords little opportunity for the postulation of ordinary tautomers or isomers with which to represent structurally the distinctions noted. Of these distinctions one of considerable importance to the structural problem is the shift of dissociation exponents from approximate equality such as might be expected of the nearly symmetrical structure assigned to leuco neutral red, to a disparity such as characterizes the dissociation exponents of neutral red itself. This change and the accompanying appearance of color suggest that the fluorescent material is some modification of leuco neutral red in which a structural asymmetry has developed. There have appeared in the literature accounts of several instances in which two forms of a given derivative of dihydrophenazine occur and attempts have been made to represent these structurally by the migration of a hydrogen atom from a bridging nitrogen to carbon ring. The evidence seems inconclusive. In particular the employment of acetylation and similar methods would, in the present instance, be futile without complete control of the physico-chemical conditions which govern the mutual interconvertibility of leuco neutral red and fluorescent material. Of such conditions we know little except for dilute aqueous solutions.

Extensive deaminization or deep-seated rupture of the molecule seems to be out of the question. We have entertained the assumptions that the "fluorescent material" is a free radical, a hydrazine or a meriquinone. What has been said seems sufficient tentatively to dispose of each of these assumptions without being reviewed with special reference to these assumptions. In speaking of the fluorescent material as an "inactive" form of leuco neutral red, we have used the term only for convenience in describing the following remarkable fact. The isolated fluorescent material when placed in neutral solution will resist oxidation for days. In solid form it will resist oxidation for years. Yet, when placed in acid solution, it becomes subject to rapid oxidation and then yields neutral red.

We thank Dr. Max Phillips and Dr. Barnett Cohen for the materials they supplied. We are particularly indebted to Dr. Leslie Hellerman and Dr. Barnett Cohen for criticism and advice.

## Summary

By avoiding so far as possible the disturbing effects of a change taking place subsequent to the formation of a mixture of neutral red and leuco neutral red, there were established potentials apparently characteristic of a reversible system. The "normal potential" at 30° was estimated to be +0.240 volt. The curve relating $P_H$ and the potentials of the half-reduced solutions, $E'_0$, has a slope $\Delta E'_0/\Delta P_H = -0.09$ in acid solution and a slope $\Delta E'_0/\Delta P_H = -0.06$ in alkaline solution. Closely crowded inflections of the curve in an intermediate zone of $P_H$ indicate dissociation exponents for reductant of 6.16 and 5.30 and for oxidant of 6.80 (approximate only).

Similar approximate data for simple neutral red are: $E_0 = +0.237$; $pK_{r_1} = 5.96$; $pK_{r_2} = 4.95$ and $pK_0 = 6.32$.

For dimethylaminomethylphenazine $E_0$ is roughly +0.208 and $\Delta E'_0/\Delta P_H = -0.06$ in acid solutions of $P_H$ number $< 5$.

Interference with stability of potentials is attributed to the formation of a substance which because of its characteristic and brilliant fluorescence is called the "fluorescent material." This was isolated in crystal form. Although it has the elementary composition attributed to leuco neutral red, it differs from leuco neutral red in the values of its dissociation constants and in other particulars. Among its several peculiar properties is its resistance to oxidation in neutral or mildly alkaline solution. In distinctly acid solution it was oxidized to neutral red. Its oxidative titration in acid solution yields a value of $E'_0$ characteristic of the neutral red system.

Because of the instability of the reversible system, neutral red can be used as an oxidation–reduction indicator only for rough comparisons. One rough comparison is made between the indications of neutral red as an oxidation–reduction indicator and electrode behavior in bacterial cultures. This comparison clarifies the "neutral red reaction" well known to bacteriologists.

The data suggest an "orthoquinone" structure for neutral red base.


BALTIMORE, MARYLAND

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## NOTE

**Preparation of Epichloro- and Epibromohydrins.**—In the preparation of 3-chloro- and 3-bromocrotonic acids[1] large amounts of epichloro- and epibromohydrins are required. Because all of the methods known for their preparation in the scientific literature give either low yields or are inconvenient, it was necessary to work out new procedures. The best yield is reported when dichlorohydrin is treated with powdered sodium hydroxide in ethereal solution,[2] but this method is not economical.

[1] Géza Braun, THIS JOURNAL, **52**, 3167 (1930).

[2] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 47,

On the other hand, very good methods are reported in the patent literature: the epichlorohydrin is obtained in high yields when dichlorohydrin is treated with calcium hydroxide[3] or with very dilute sodium hydroxide solution.[4] The calcium hydroxide method seemed to be more advantageous, therefore this process was modified to laboratory conditions.

(a) The conversion of dichlorohydrin into epichlorohydrin with calcium hydroxide in the presence of water takes place easily even at room temperature. A number of experiments were carried out under various conditions and it was found that this conversion is about 75% in one operation, but it is not advisable to complete the reaction by raising the temperature or loss in epichlorohydrin will occur; it is best to remove the epichlorohydrin by fractional distillation and treat the residue again with calcium hydroxide. This can easily be done without loss of time, for the operations are very simple. The yield of epichlorohydrin is as high as 80%, in larger amount (4–5 kg.) up to 90% of the theoretical.

(b) The conversion of dibromohydrin with calcium hydroxide into epibromohydrin in the manner described above is much simpler than that of dichlorohydrin. The operation is almost complete in one treatment, and the yield of epibromohydrin is as high as 90% of the theoretical.

## Experimental Part

(a) **Epichlorohydrin.**—In a 5-liter round-bottomed flask 1350 g. (1 liter) of dichlorohydrin, 840 g. of calcium hydroxide (technical, 88%) and 840 cc. of water were vigorously shaken for fifteen minutes at room temperature. The mixture was a thick paste at the beginning, but the epichlorohydrin soon separated from the calcium salts as a thin liquid. No formation of heat was observed. Then the mixture was distilled at first under 40–50 mm., then under 10 mm. pressure, gradually raising the temperature up to 100°. The receiver was cooled with ice and salt to −2° to prevent loss of epichlorohydrin. The distillate was transferred into a separatory funnel, the aqueous layer poured back into the distilling flask and the distillation repeated as above. A third distillation in a similar manner still yielded some epichlorohydrin. The united lower layers of the distillates (570 + 220 + 20 = 810 cc.) were fractionated under 50 mm. pressure at 75° and separated into two fractions, (a) distillate and (b) residue. The residue (about 160–180 cc.) contained a large percentage of dichlorohydrin and was poured back into the original distilling flask, together with 150 cc. of water, and distilled once under reduced pressure as above. The lower layer of the distillate was united with fraction (a) and distilled under reduced or ordinary pressure.

From the first distillate the water was removed, it was dried with an-

[3] Griesheim, German Patent 246,242.

[4] Bayer, German Patent 239,077.

hydrous sodium sulfate, poured back into the distilling flask and the crude epichlorohydrin thus freed from water fractionated again. After a small forerun the pure epichlorohydrin distilled at 30–32° under 10 mm. pressure; the yield was 770 g. of epichlorohydrin or 80% of the theoretical. The epichlorohydrin thus obtained boiled at 115–117° and had a specific gravity of 1.18 at 20°.

(b) **Epibromohydrin.**—One liter (2140 g.) of dibromohydrin was suspended in 1.5 liters of water and then gradually under shaking 420 g. of calcium hydroxide was added in the course of fifteen minutes. Then 420 g. of calcium hydroxide was added at once and the epibromohydrin distilled under reduced pressure in the same manner as is described in the case of epichlorohydrin. The united lower layers of two distillations (690 + 70 = 760 cc.) were fractionated under 50 mm. pressure and the medium fraction, after drying with anhydrous sodium sulfate, fractionated again. The yield of epibromohydrin (b. p. 61–62° under 50 mm. pressure or 134–136° at ordinary pressure) was 1200 g. or 90% of the theoretical. The product had a specific gravity of 1.665.

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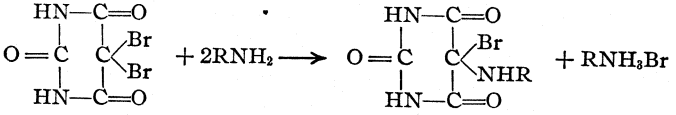
RECEIVED OCTOBER 15, 1931
PUBLISHED MARCH 5, 1932

## COMMUNICATIONS TO THE EDITOR

### THE REACTION OF DIBROMOBARBITURIC ACID WITH AMINES

*Sir:*

In a recent communication Nightingale and Schaefer[1] describe the reaction of 5,5-dibromobarbituric acid with primary and secondary amines. The reaction is said to yield a series of 5-bromo-7-alkyl uramils.



Such a reaction seems improbable in view of the general properties of the class of "persubstituted" halogen compounds.[2] Such compounds act as brominating agents, the active halogen being replaced by hydrogen. To quote a single example, bromonitromalonic ester reacts with dimethylamine to form the amine salt of nitromalonic ester and N-bromodimethylamine.[3] Baeyer[4] and Biltz and Hamburger[5] obtained the ammonium

[1] Nightingale and Schaefer, THIS JOURNAL, **54**, 236 (1932).

[2] *Cf.* a summary by Schmidt, Ascherl and von Knilling, *Ber.*, **59**, 1876 (1926), which includes over seventy references to the literature.

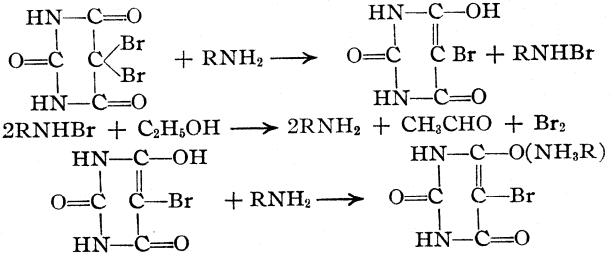
[3] Willstätter and Hottenroth, *Ber.*, **37**, 1776 (1904).

[4] A. Baeyer, *Ann.*, **130**, 134 (1864).

[5] Biltz and Hamburger, *Ber.*, **49**, 641 (1916).

salt of monobromobarbituric acid on treating dibromobarbituric acid with aqueous ammonia.

From a consideration of the above evidence it seemed probable that the compounds reported by Nightingale and Schaefer were not 5-bromo-7-alkyl uramils, but merely the amine salts of 5-bromobarbituric acid. The authors mention the fact that their products are decomposed by alkalies with the liberation of the amine. This would be a very unusual reaction for a substituted uramil, since uramil itself is hydrolyzed slowly by alkalies into urea and aminomalonic acid. The liberation of the amine would be expected, however, on treating alkyl ammonium 5-bromobarbiturates with alkali. These salts lack but two hydrogen atoms of being isomeric with the uramils; consequently the nitrogen and bromine analyses which constitute the only proof of structure offered by Nightingale and Schaefer could be explained by either formula. From results reported[3] in the literature it would seem that the formation of these salts could be accounted for by the reactions




In order to establish the structure of the compounds prepared by Nightingale and Schaefer their work was repeated with ethylamine, di-*n*-propylamine and di-*n*-amylamine. The products agreed in physical properties with those which they reported, and all of them were decomposed immediately by cold 10% sodium hydroxide with the liberation of the amine. Such a rapid reaction is characteristic of the liberation of an amine from a salt, and not of the splitting of a nitrogen to carbon linkage. The reaction was carried out quantitatively in one case. The di-*n*-propylamine salt (1 g.) was treated with an excess of cold 20% sodium hydroxide and the free amine extracted with ether. The amine was extracted from the ether solution with dilute hydrochloric acid, the extract being placed in a Kjeldahl apparatus and made alkaline with 20% sodium hydroxide. The amine was determined by distillation into an excess of standard acid: required, 32.47 cc. of 0.1 *N* sulfuric acid, or 100.03% calcd. The titrated solution was evaporated to dryness and dipropylamine dipropyldithiocarbamate prepared as a derivative; m. p. 118–118.5°, mixed with a known

[6] Reaction 2 is not essential to the formation of the salts, but merely indicates the method by which the amine is regenerated; *cf.* Biltz and Behrens, *Ber.*, **43**, 1984 (1910); Berg, *Ann. chim.*, (7) **3**, 339 (1894).

specimen gave no depression. Monobromobarbituric acid was obtained from each of the salts by a procedure similar to that employed by Biltz and Hamburger[5] with the ammonium salt. Yields of 30–50% of pure 5-bromobarbituric acid were obtained; m. p. 215–216°;[7] Br calcd., 38.61; found, 38.90. The loss is due to the solubility of the sodium salt and the instability of 5-bromobarbituric acid in aqueous solution.[7]

The products obtained by Nightingale and Schaefer have thus been demonstrated to be alkyl ammonium 5-bromobarbiturates. The "dark tarry oils" which they obtained with dibromobarbituric acid and aromatic amines were formed in a similar bromination process; such experiments have been reported previously in the literature. Dibromobarbituric acid and aniline give monobromobarbituric acid and *p*-bromoaniline,[8] while with dimethylaniline monobromobarbituric acid and *p*-bromodimethylaniline are obtained.[9]

[7] Bock, *Ber.*, **55**, 3401 (1922).

[8] Conrad and Reinbach, *ibid.*, **35**, 522 (1902).

[9] Gupta and Thorpe, *J. Chem. Soc.*, **121**, 1898 (1922).

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PUBLISHED MARCH 5, 1932

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## CESIUM FILMS ON TUNGSTEN

*Sir:*

When cesium atoms strike a tungsten filament at high temperature (filament surrounded by negatively charged cylinder), every atom is ionized. At lower temperature the number of adsorbed atoms (adatoms) per unit area ($\sigma$) can be measured by flashing the filament and allowing the evaporated atoms to strike a second parallel filament from which they evaporate as ions. The potentials of the two filaments are so chosen that no ions escape from the first but all escape from the second. A galvanometer ballistic kick gives a quantitative determination of $\sigma$.

Dr. J. Bradshaw Taylor has developed this method for measuring the rates of evaporation of atoms ($\nu_a$), ions ($\nu_p$) and electrons ($\nu_e$) as functions of $\sigma$ and $T$. The following conclusions are drawn.

The tungsten surface, after considerable heating at 2800°K., is homogeneous, except that a small fraction (0.0050) can hold adatoms more firmly than the rest. With rising pressure, and a filament at 1100–1200°K., the first atoms are adsorbed on this active surface, which becomes saturated before 0.5% of the remaining surface is occupied. The active spots are separate spaces holding one atom each from which the heat of evaporation is 80 Kg. cal. per g. atom. The following refers to the homogeneous surface.

With low filament temperatures and high pressures, $\sigma$ reaches a limit $\sigma_1 = 3.563 \times 10^{14}$ atoms per sq. cm. of true surface (34% greater than apparent surface) corresponding to a monatomic film with one Cs atom for four tungsten atoms. The electron emission at constant $T$ reaches a maximum at $\Theta = \sigma/\sigma_1 = 0.67$.

From the data on $\nu_a$, by Gibbs' adsorption equation, the spreading force $F$ (dynes. cm.$^{-1}$) can be calculated and the two-dimensional equation of state is $F = \sigma_1 kT\Theta/(1 - \Theta) + F'$. Using the virial of the force $f$ acting at a distance $r$ between adatoms: $F' = 0.25\ \sigma\Sigma(rf)$. The forces are strong repulsove forces varying as $r^{-4}$. The adatoms constitute dipoles, whose moment $M$ decreases as $\Theta$ increases by the depolarizing force of neighboring adatoms. It is deduced theoretically (without adjustable parameters) that

$$F' = 3.338\ M^2\sigma^{5/2} + 1.531 \times 10^{-5}\ M^{4/3}T^{1/3}I\sigma^2$$

$I$ being an integral which decreases from 0.893 to 0 as $\Theta$ increases from 0 to 1. From experimental values of $F$ it is found that $M = 16.3 \times 10^{-18}$ at $\Theta = 0$, this coefficient decreasing to 9.8 at $\Theta = 0.3$ and 7.6 at $\Theta = 0.6$. The contact potential $V = 2\pi\sigma M$ can thus be calculated from $\nu_a$, agreeing with direct measurements and with values calculated from

$$\ln \nu_e = 63.44 - (11606/T)(4.760 - V)$$

$V$ being in volts.

The experimental values of $\nu_a$ give

$$\ln[\nu_a(1 - \Theta)/\Theta] - 1/(1 - \Theta) = A - B/T$$

where

$$A = 61 + 4.8\,\Theta - 2.4\,\Theta^2$$

and

$$B = 32380/(1 + 0.714\,\Theta)$$

The thermodynamic relation

$$\ln(2\nu_p) = \ln \nu_a + (11606/T)(V_w - V_i - V)$$

gives $\nu_p$ (in agreement with experiment), where $V_i = 3.874$ volts (ionizing potential of Cs) and $V_w = 4.622$ (work function for W).

From these equations $\nu_a$, $\nu_e$, $\nu_p$ and $V$ are calculable, as functions of $T$ and $\Theta$ (up to 0.65), from a curve giving $M(\Theta)$ and from $V_i$, $V_w$ and the heat of evaporation of adatoms from a bare tungsten surface, 63.5 Kg. cal. per g. atom (2.757 volts).

IRVING LANGMUIR

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## THE HYDROGEN NUCLEUS OF MASS 2 (ISOHYDROGEN NUCLEUS $p_2e$) AS A UNIT IN ATOM BUILDING

*Sir:*

On the basis of the fact that the formula[1] $(p_2e)_z$ represents the most abundant atomic nuclei, and because the formula $p_2e$ represents the general increment in composition of nuclei of odd atomic weight, the writer has considered the nuclear group $p_2e$ to play a fundamental role in atom building. Also such a particle was supposed to possess a great advantage over the alpha particle as a unit in atom building since, on account of its smaller charge, it much more readily penetrates the potential wall around a complex nucleus. A part of this point of view is presented in fragmentary quotations from papers published[2] in 1921 and 1923. "Electron groups in which one negative electron alone is present may be even more fundamental in a certain sense" than the $p_2e_4$ group or alpha particle, "especially since the group $p_2e$ corresponds to the minimum value of $N/P$ for a nucleus stable both with respect to disintegration by ordinary means, and moderately stable with regard to aggregation" (*i. e.*, union with other nuclei). "If $p_2e$ is the fundamental group, as the general considerations suggest, then its low abundance may be explained as due to the pairing of the negative electrons, two $p_2e$ groups changing into one alpha particle." "The first step in the formation of an alpha particle may be the union of two protons with one electron to form the group $p_2e$, which is very difficult to break up, but readily unites with a like group to form an alpha particle. Sometimes it may add to a complex nucleus." The newer data give additional support to this idea. All atomic species may be divided into four series (Table I).

TABLE I

1. Even ($2R$) Series
   $(p_2e)_R e_S$
   A. Thorium ($4\,M$)
      $R$ = even, $S$ = even
   B. Uranium
      $R$ = odd, $S$ = odd
   $R$, $S$, $M$ = whole numbers

2. Odd ($2R + 1$) Series
   $(p_2e)_R(pe)e_S$
   $R$ = either odd or even
   if $S$ = odd or even
   A. Beryllium ($4\,M + 1$)
   B. Actinium (?) ($4\,M + 3$)

The matching or non-matching of $R$ and $S$ in evenness or oddness is of fundamental importance.

TABLE II

DIFFERENCE OF COMPOSITION ON ANY LEVEL OF CONSTANT ISOTOPIC NUMBER ($S$ = CONSTANT)

| Level | Even series | Odd series |
|---|---|---|
| Zero | $p_2e$ | $p_2e$ |
| 1 to 26 | $p_4e_2$ (= $\alpha$) | $p_2e$ |

[1] $p$ = a proton, $e$ = an electron, $z$ = atomic number, $P$ = atomic weight or number of nuclear protons, $N$ = number of nuclear electrons.

[2] *Phil. Mag.*, **42**, 334 (1921); THIS JOURNAL, **45**, 1426–1433 (1923).

The even series are merely extensions of the radioactive series, *since any level represents a series of alpha changes* (Fig. 1 and Table II).

*All levels of the odd, and the zero level of the even, series exhibit the difference* $p_2e$.

It is remarkable that every possible multiple of $p_2e$ from 1 to 8 is now known.[3]

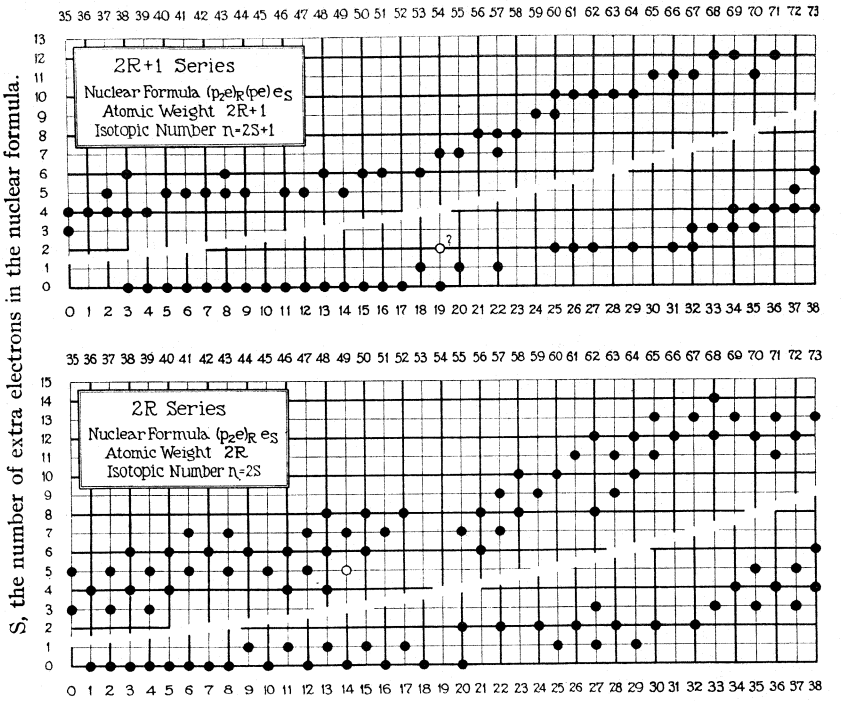


Fig. 1.—$R$, the number of $p_2e$ units in the nuclear formula (atomic number $Z=R-S$).

The isohydrogen nucleus may be formed by the collision of a proton with a permanent or temporary neutron ($pe$), or by a three body single collision. In the latter case the wave length emitted should be about 0.001 Å. The nuclear spin of $p_2e$ is probably zero, but may be unity in units $h/2\pi$, while that of the neutron should be $1/2$. There is much evidence which indicates that in the nucleus groups of the composition $p_2e$ do not, in general, remain independent, but that they merge by doubling into units of the composition of alpha particles.

[3] Recent discoveries are: beryllium isotope $(p_2e)_3$, Watson and Parker, *Phys. Rev.*, **37**, 167 (1931); and a higher isotope of hydrogen, F. Allison (American Chemical Society meeting, September, 1931), and about 1/4000 of hydrogen of mass 2 in hydrogen, Urey, Brickwedde and Murphy, *Phys. Rev.*, **39**, 154 (1932).

The extra electrons of the formulas (Fig. 1) are therefore not the "extra" or "loose" electrons of the nuclues. The correct values of these are given in another paper (*Phys. Rev.*, **38**, 1280–1282 (1931).

It may be supposed that in the building up of complex atomic nuclei the following particles may attach themselves to an atomic nucleus provided they penetrate its potential wall: protons, electrons, neutrons if they exist, $p_2e$ particles and alpha particles.

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UNIVERSITY OF CHICAGO
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WILLIAM D. HARKINS

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## CRYSTALLIZATION VELOCITIES

*Sir:*

Although it has long been known that the rate of crystallization from supercooled melts is greatly dependent on the particular compound used, the effect of molecular symmetry has not been investigated up to the present time. If there is such an effect, it should be most easily discoverable with organic compounds, whose structures may be postulated from x-ray and dipole moment measurements.

Recent measurements here on the linear crystallization velocity indicate that the symmetry of the molecule largely determines the rate of transition from liquid to solid. The maximum linear velocities of the most illustrative examples so far measured are tabulated.

MAXIMUM LINEAR VELOCITIES

| Compound | Rate in mm. per minute | Melting point, °C. | Supercooling, °C. |
|---|---|---|---|
| *o*-Dichlorobenzene | 2,200 | −17.6 | 25 |
| *m*-Dichlorobenzene | 700 | −24.8 | 25 |
| *p*-Dichlorobenzene | 20,000 | 52.9 | 25 |
| 1,2,4-Trichlorobenzene | 25 | 17 | 25 |
| 1,3,5-Trichlorobenzene | 7,500 | 63.4 | 26 |
| 1,1,2-Triphenylethane | Less than 1 | 54.0 | 50 |
| 1,1,1-Triphenylethane | 77 | 94.8 | 33 |
| 1,2-Diphenylethane | 700 | 51.2 | 34 |
| 1,1-Diphenylethylene | 16 | 8.2 | 25 |
| Diphenylmethane | 530 | 25.1 | 27 |
| Triphenylmethane | 27 | 93.6 | 29 |

In view of the recent revival of interest in the subject of crystallization, this preliminary report is being given at this time to avoid possible wasteful duplication. It is planned to discuss the complete results in a paper later.

DEPARTMENT OF CHEMISTRY
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MAURICE E. KRAHL

RECEIVED FEBRUARY 12, 1932
PUBLISHED MARCH 5, 1932

## NEW BOOKS

**Smith's Introductory College Chemistry.** By JAMES KENDALL, F.R.S., Professor of Chemistry in the University of Edinburgh. The Century Co., 353 Fourth Ave., New York, 1931. xii + 555 pp. Illustrated. 13.5 × 20.5 cm. Price, $3.25.

This text maintains the traditional Smith arrangement. It will prove just as effective in its field as the other Smith texts.

The arrangement of facts followed by theory throughout the book interspersed here and there with problems illustrating the principles learned is the only way to teach a science. The Smith texts have always done this very well. In that respect this text is just as good as the others.

In abbreviating the College Chemistry nothing essential has been omitted. The text ought to be well received in colleges where the larger volume seemed to contain too much material for the type of course offered.

In regard to the Smith texts as a whole it seems to me that Kendall ought to have the courage of the Founder and introduce the subject by his chapters on the Periodic System and the structure of the atom if he wishes these texts to maintain the supremacy established by Smith when he revolutionized the teaching of General Chemistry in 1906. The time is ripe for another jolt in first year College Chemistry.

JOHN B. ZINN

**Qualitative Chemical Analysis from the Standpoint of the Laws of Equilibrium and the Ionization Theory.** By LOUIS J. CURTMAN, Associate Professor of Chemistry, The College of the City of New York. The Macmillan Company, 60 Fifth Ave., New York, 1931. x + 539 pp. Illustrated. 14.5 × 22.5 cm. Price, $4.00.

This textbook is planned for a full year's course in qualitative analysis. It is divided into five parts.

The first part, 137 pages, is devoted to Theory and Special Apparatus. It includes much material usually found only in treatises on physical chemistry. Hydrogen Electrode, Buffered Solutions, Concentration Cells, Atomic Structure The Centrifuge, and Werner's Coördination Theory are some of these. All such included topics are treated in such a manner as to show their applications to qualitative analysis. The treatment of ionization is good. The Theory of Debye and Hückel is presented but the useful parts of the older theory are not omitted. Writing equations, including those representing oxidation–reduction reactions, and the solution of problems are carefully and fully explained. The connection between the statement of the theory and the mathematical expressions for the mass law and the solubility product is not given very fully.

The 112 pages devoted to The Metal Ions consists of descriptions of reactions significant in qualitative analysis, equations to represent these reactions and theoretical explanations of the changes which occur.

The 20-page section entitled Calculations is devoted entirely to calcula-

tions connected with standard solutions. However, problems and questions to test the understanding of other calculations appear in appropriate places through the book.

The fourth part, Laboratory Work, includes: directions for making apparatus, a list of all chemicals and the quantity needed by a student in the course, directions for the preparation of an individual kit for each student including the cabinet, bottles, making the solutions and directions for preliminary experiments and analysis for cations.

The fifth section deals with preliminary experiments and analysis for acid ions and includes a plan for a systematic analysis. The acids are identified first because so many acid ions interfere with cation analysis.

The analysis includes tests for 25 cations and 25 anions. The 39 figures are well chosen and very helpful. Eighteen numbered tables of data and many more unnumbered tabulations furnish an enormous amount of information relevant to analysis. The 16-page table of analytical constants is especially valuable. The tables showing the dissociation constants of complex ions and the equivalent conductance of ions at infinite dilution suggest the wide range covered. The book contains an enormous amount of well-chosen and well-presented material on qualitative analysis. It should be extremely valuable to any teacher of qualitative analysis. Teachers might omit some parts of the material presented, but the text is too comprehensive for courses shorter than two quarters.

F. E. BROWN

**Lehrbuch der anorganischen Chemie. (Textbook of Inorganic Chemistry.)** By Dr. HEINRICH REMY, Professor at the University of Hamburg. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1931. Vol. I, xxii + 718 pp. 92 figs. Vol. II, xvi + 450 pp. 32 figs. 15 × 24 cm. Price, Vol. I, RM. 20; bound, RM. 23. Vol. II, RM. 14; bound, RM. 16.80.

This new textbook is a significant attempt at an instructive presentation of the most recent aspects of inorganic chemistry. The object and method of the author are stated in his preface as follows: "The present book is designed to afford a comprehensive picture of the whole field of inorganic chemistry. This is to be effected by a presentation of the body of facts which have resulted from observation and experimentation, with particular emphasis on the laws which connect them, and the causal relationships which are deducible from them."

The book assumes a general knowledge of elementary chemistry and physics. The author starts with a careful description of the Periodic System, which thereafter serves as the guiding principle in the arrangement and treatment of the chemical elements and their compounds. The first volume is devoted to the elements of the main groups of the periodic system, that is, to the elements whose atomic numbers are 1–3 units greater or 4–1

units smaller than the atomic number of an inert gas. The second volume covers the other elements, that is, the elements of the transition groups (Nebengruppen) and the rare earths (lanthanide group).

Hydrogen is the first element to be discussed, and it serves for the introduction and elucidation of such general matters as electrolysis, electrochemical potential, overvoltage, the mass law, the reaction isochore, strong and weak electrolytes, series spectra, and Bohr's theory. The chapter on the inert gases comes next, and this is followed by a chapter on Kossel's and Lewis' theories of valence. A chapter on the alkali metals is followed by one of 34 pages on crystal structure and x-rays. A similar intercalation of theoretical discussion at appropriate points occurs throughout the remainder of the treatise. It therefore affords a thorough presentation not only of the facts of inorganic chemistry, but also of the theories of general chemistry. A similar procedure has been adopted in certain previous textbooks, but this represents the most up-to-date attempt in this direction.

The descriptive matter is presented from a thoroughly modern point of view. Crystal structure data abound and constant application is made of the coördination theory. The chemistry of many really important elements such as titanium, zirconium, vanadium, molybdenum, tungsten and uranium which usually is given scant attention except in the very largest treatises is here presented very fully. There is also an exceptionally clear and satisfactory chapter on the rare earths.

Every fact of inorganic chemistry that one might like to have available cannot, of course, be included in two medium-sized volumes. Thus, details as to methods of preparation of substances, the industrial and technical aspects of inorganic chemistry, and in particular the metallurgy of the common metals are not very adequately covered. The book should, however, be most useful and instructive to students and teachers of inorganic chemistry who wish to secure a broad and up-to-date knowledge of both the descriptive and theoretical aspects of their subject.

ARTHUR B. LAMB

**Bandenspektren. (Band Spectra.)** By Dr. W. WEIZEL, Professor at the Technical High School of Karlsruhe. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1931. xiii + 461 pp. 139 figs. 17.5 × 25 cm. Price, RM. 43; bound, RM. 45.

This book on molecular spectra is issued as the first supplementary volume to the Wien–Harms "Handbuch der experimentellen Physik." The subject had already been treated in Vol. 22 of the Handbuch, but its subsequent development has been so rapid that the editors thought it advisable to publish this new and fuller account. This was especially true because the theory of band spectra has now become a relatively complete

and stable structure, in so far as it concerns diatomic molecules. Weizel's book is masterly in treatment, and in the reviewer's opinion is by far the best and most complete yet published on the subject.

The book is divided into an introduction and four chapters. In the first chapter (143 pages) the theory of the energy levels of diatomic molecules is developed in a very clear and comprehensive manner, largely in terms of "a somewhat primitive" form of wave mechanics. The second chapter (66 pages) is entitled "The structure of the band spectra of diatomic molecules," and includes a discussion of intensity relations. Chapter III (11 pages) deals briefly but helpfully with the theory of polyatomic molecules.

After laying this solid theoretical foundation, the author uses it in the fourth chapter (222 pages) to classify and explain what is known experimentally about the spectra of diatomic and simple polyatomic molecules. The polyatomic molecules occupy 31 of the 222 pages. This chapter contains an adequate review of practically all important results on these spectra obtained up to June 1, 1931. The chapter is divided into sections, for example: the spectra of hydrogen ($H_2$); the band spectra of metal vapors; band spectra of diatomic hydrides; spectra of the oxides; spectra of molecules of the type $XY_2$ ($CO_2$, $NO_2$, $SO_2$, etc.); spectra of organic compounds. Each such section ends with an extensive bibliography of the important literature, omitting, however, older references which have been superseded by more recent work. Nearly every section contains complete tables of molecular constants resulting from the analysis of the band spectra discussed in that section. These data are, however, admittedly not always critical, especially in the case of energies of dissociation, and there are occasional errors and omissions. Numerous convenient tables of wave length or frequency data are included. The book contains numerous helpful explanatory figures.

Chemical applications of band spectrum data are not stressed: for example, very little is said about the problem of chemical binding and valence, and little or nothing about the use of band spectrum data in calculating specific heats and entropies, or in estimating heats of activation.

ROBERT S. MULLIKEN

**Physical Chemistry for Colleges.** By E. B. MILLARD, Professor of Physical Chemistry, Massachusetts Institute of Technology. Third edition. The McGraw-Hill Book Company, Inc., 370 Seventh Ave., New York, 1931. ix + 522 pp. Illustrated. 14.5 × 21 cm. Price, $3.75.

The first edition of this book appeared in 1921 and the second edition in 1926. The present third edition contains some 111 pages more than the first edition and 64 more than the second. Errors, which were fairly numerous in the first edition, have been largely eliminated; a few still

remain. As stated in the preface to the first edition, "The limitations of the orthodox laws of physical chemistry have been emphasized more than is commonly done in beginning courses in physical chemistry."

All the more important phases of physical chemistry are included in this book. The inclusion of so many topics in a book of this size will be criticized by some as having resulted in a too highly condensed treatment of certain important topics, such, for example, as that of liquefaction of gases, which is confined to a single short paragraph. It is the opinion of the reviewer that the chapter on properties of substances in the liquid state could be improved by a slight expansion in which the kinetic theory as related to this state would receive ample discussion. A more rigorous treatment of the evaluation of boiling point constants and freezing point constants would be helpful. This is especially desirable since the values for the constants as given in the tables cannot be obtained by use of the methods described in the text. In the chapter on thermochemistry confusion would be avoided by adopting a convention to be observed throughout in referring to heats of combustion. As it is, one does not always know whether the author refers to heats of combustion at constant pressure or at constant volume. This cannot help but be troublesome to the student in his attempts to solve the problems given in this chapter.

The chapters on chemical kinetics, on atomic structure and on heterogeneous equilibrium have been revised. The latter has been distinctly improved by the inclusion of diagrams and discussions which give a desirably complete and condensed treatment of this important chapter. A new chapter on photochemical change has been added. Of outstanding value are the excellent groups of questions and problems given at the end of each chapter. Important additions of these have been made in the present edition. On the whole this new, third edition represents a distinct improvement over earlier editions, is a book which possesses real merit, and deserves a prominent place among the better texts in physical chemistry.

F. E. BARTELL

**Molecular Rays.** By RONALD G. J. FRASER, Ph.D. (Aberdeen). The Macmillan Company, 60 Fifth Ave., New York, 1931. xiii + 204 pp. 14.5 × 22 cm. Price, $3.75.

The author of this excellent book, "Molecular Rays" (in the Cambridge Series of Physical Chemistry), has himself spent three years in Professor Stern's laboratory. With his background of intimate acquaintance with the details of the molecular ray technique, Dr. Fraser attempts to give an account of the fundamentals of this new field of research. The author succeeds so well that one cannot read the pages of this book without catching some of the inspiration of the subject. Those who read will appreciate, perhaps for the first time, the beauty and the power of the molecular ray

method, and will become firm believers in the marvelous possibilities which undoubtedly are to attend its future development.

The book, with a two-page Foreword by Professor Stern, is composed of seven chapters, headed as follows: The Production and Measurement of Molecular Rays; Gas Kinetics; Problems of the Gas–Solid Interface; The Diffraction of Molecular Rays; The Magnetic Deviation of Molecular Rays; The Electric Deviation of Molecular Rays; Chemical Equilibria, Ionization, Spectroscopic Applications. An appendix gives a brief discussion of the relationships among, and conversion factors for, average velocity, root mean square velocity and the most probable velocity. Both an author and a subject index are supplied.

"The book has been written strictly from the experimental standpoint, and is intended primarily to give a balanced survey of the whole field rather than a minute examination of its separate parts" (from Author's Preface). The book is written in clear, forceful English, with enough detailed but simple mathematical development to make the important equations clear. Particularly attractive are the author's treatments of methods of "detecting" molecular beams, and of problems involved when molecular beams impinge on solid surfaces, including the effects, scattering, reflection, adsorption, condensation and diffraction. Chemists will be interested to note, in Chapter 7, the critical judgment which Dr. Fraser passes on the three attempts which have been made to test the radiation hypothesis by using a collision-free molecular ray, namely, the experiments of Kröger with iodine, Mayer with pinene and Rice, Urey and Washburne with nitrogen pentoxide. The author gives good reasons for doubting whether any of these attempts really establishes the conclusion which it is generally supposed has been established, although the author predicts that the molecular ray method of studying chemical reactions may yet prove of value.

Chemists and physicists who expect to follow the future literature accounts of developments in this most fascinating field of the molecular ray would do well to digest the contents of Dr. Fraser's book.

EDWARD MACK, JR.

**Elektrochemie der Kolloide. (Electrochemistry of Colloids.)** By Prof. Dr. WOLFGANG PAULI AND Dr. EMERICH VALKÓ. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1929. xii + 647 pp. Illustrated. 16 × 24 cm. Price, $17.00.

Pauli and Valkó have produced a book which undoubtedly takes a place amongst the chief works on colloid science. It is always of great service to science when a leading investigator who has been active during the greater part of the development of a subject puts together his experience and records his reasoned judgment upon the work of his contemporaries.

The book comprises several very different parts, beginning with a 56-

page introduction dealing with such topics as solutions, valency, etc., at which most readers will boggle on account of its elementary nature but which nevertheless proves useful for reference in elucidating the personal standpoint of the authors. This is followed by a section comprising at least a quarter of the book in which the attempt is made to discuss from one comprehensive standpoint all electrolytes and colloids, basing the treatment upon the theory of interionic attraction and including rather complete references to all those who have contributed toward the composite picture built up by the authors.

This monographic dissertation is of indispensable importance to research workers, alike in the fields of colloids and of dissociation theory. Never again will it be possible to give an adequate account of one of these subjects without considering the other. The treatment, however, is only for the advanced student or research worker because insufficient care has been taken to keep the matter precise and explicit or even in some cases to define the terms and the mathematical symbols employed. It is necessary, therefore, to refer to the original literature whilst reading this section. Indeed throughout it is evident that the subject of colloids has not yet wholly freed itself from the reproach of ambiguity and confusion of thought.

In one thing the reviewer is disappointed, namely, the assumption that the theory of strong electrolytes needs merely to be applied rather than to be modified in view of the incomparably wider range of experimental behavior brought under consideration. It seems more reasonable to expect that much is to be learned from the behavior of charged colloids and their accompanying ions which could hardly be suspected or established from the contemplation of the properties of potassium chloride. Rather than, for example, to assume that all possible electrolytic material contained in a colloidal particle (such as FeOCl in a ferric hydroxide sol) is 100 per cent. dissociated even though it may not take any part in conductivity or osmotic pressure and migrates as a whole with the colloidal particle in an electric field, it is surely better to attempt to learn from such cases in how far the assumption of complete dissociation is justified. It is logical to ponder this, and such observations as the breakdown of the principle of ionic strength for such polyvalent colloids as soap, and then to apply the results in appropriate measure to ordinary electrolytes. The authors do not discriminate between the arbitrary ephemeral conception of 100 per cent. dissociation and the physical phenomena of interionic attraction which are permanently real and important even if their present formulation should prove to be only approximate.

The authors again do not sufficiently emphasize the fictitious nature of many of the mathematical expressions in which electricity is treated as a continuum rather than as electronic, and no regard at all is paid to real atomic, molecular and colloidal dimensions and the localized nature of

charges and valencies. Consider, for example, a nonylate ion, a large amino acid, a zwitter ion or a plane surface with charges spaced widely apart, in comparison with the fictitious assumption of continuous distribution of the single charge of electricity as well as the opposing charge regarded as spread out in either a uniform sphere or plane, implicit in some of the formulations. Often after describing a point of view or a formulation, the authors do express their misgivings but unfortunately they do not go back and revise the treatment accordingly.

These criticisms which the reviewer is impelled to make are not intended to detract from the important achievement of showing once for all the essential identity of the operative processes of electrochemistry, whether they be termed colloid science, electrokinetics, electrocapillarity, electromotive force or theory of electrolytes.

There follow next 200 pages of general description of colloid behavior, simply and comprehensively presented, although important chapters such as Brownian movement, viscosity and structure are only most briefly referred to. Then comes one of the most valuable parts of the book, namely, the 100-page summary of the authors' knowledge of the proteins. The book then concludes with much briefer summaries devoted to metal sols, silicic acid, stannic acid, hydroxides, sulfides and sulfur, soaps, dyes and carbohydrates in their behavior as colloids; to these students and investigators may be referred for an authoritative and in many cases first hand account.

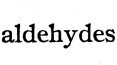
JAMES W. MCBAIN

**Thermochemie.** (Thermochemistry.) By Dr. W. SWIETOSLAWSKI, Professor of Physical Chemistry at the Polytechnical High School of Warsaw. Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany, 1928. xi + 253 pp. 28 figs. 17 × 25 cm.

The first chapter in this book is on general calorimetry; and though relatively brief, provides an unusually satisfactory introduction to research in this field, particularly because it is not only a clear but also a suggestive exposition which tends to direct the reader's thought toward a critical evaluation of procedures. It does not, however, go far enough in this direction to serve the purposes of the fully prepared experimentalist, since though published in 1928, it omits all reference to the systematic studies of error that have been published in America during the last decade, a neglect of which might well impair very seriously the value of any work in this field which aimed at high precision. The careful worker who uses this book had better, therefore, supplement it with White's "The Modern Calorimeter" (A. C. S. Monograph, 1928) where calorimetric precision is adequately discussed.

The general treatment of calorimetry is continued by descriptions

of the special techniques employed in measuring specific heats, heats of fusion and evaporation, of solution and dilution; and is followed by a sound and especially suggestive discussion of the methods of thermochemistry proper: which include procedures for testing the completion of reaction, absence of superimposed effects both physical and chemical, and variability of thermal effects caused by the use of different neutral media, varying excess of one ingredient, indeterminate contamination and so on. This part of the work, which deals with insidious sources of error in chemical calorimetry that too frequently escape the notice of physicists, is for purposes of instruction important. It is followed by a lengthy discussion of the thermochemist's favorite method of bomb calorimetry, which leads to an interesting critique of the uncertainties and errors characteristic of past work on heats of combustion, and ends with an attempt to evaluate the probable precision of the more important earlier data derived from determinations of this heat. Much good advice is incidentally included in this discussion.

The second half of the book is an analysis of thermochemical data. The author discusses here the principles whereby these data, especially those of heats of combustion, may be made to yield knowledge about the characteristic heats of simple atomic combinations and the variability of these with differences of structure in the molecular species where they occur as characteristic groups. He then applies these principles systematically, by the use of critically evaluated data, to the determination of the "thermal characteristics" or heats of formation of the groups which define all the most important genera of organic compounds: C—C and C—H, C=C, C≡C in hydrocarbons both aliphatic and cyclic; C=O, C—O—C, C—OH,  in aldehydes and ketones, alcohols and esters; and so on, including the characteristic radicals of amines, cyanides, amides, nitro-bodies and other genera. The discussion is detailed, thorough-going and convincing, and gives to this part of the work the character of critical research rather than that of a mere summary exposition. The author discovers in the total mass of data which he has laboriously correlated, only two fairly invariable "thermal characteristics:" those namely of C—C and C—H in the saturated hydrocarbons; but he establishes, so far as the data permit, the ranges of the variability of those for other groups and, by intercomparisons, the characteristic effects upon them of increasing molecular mass and of certain types of structure. His summaries thus demonstrate on the one hand the extreme hazard of calculating from such characteristics (unless very roughly indeed) any but a very limited group of heats of reaction; but on the other, they clearly show in a qualitative way the typical influence upon these characteristics of certain molecular configurations. As a critique of the present position of thermo-

chemical theory and as a stimulation to further work in this difficult field—which is thus shown to be as yet only made ready for intensive cultivation—this section of the work is particularly valuable.

The book closes with tentative applications of the data obtained by the preceding analysis of combustion heats to the determination of heats of atomic combinations of C, H, O, N, S and the halogens, to the calculations of heats of molecular transposition and of dissociation, and with a final discussion of general import.

FREDERICK BARRY

**An Introduction to Organic Chemistry.** By ROGER J. WILLIAMS, Professor of Chemistry, University of Oregon. Second edition. D. Van Nostrand Company, Inc., 250 Fourth Ave., New York, 1931. xi + 585 pp. 14 × 22.5 cm. Price, $3.50.

The second edition of this popular text is revised, not rewritten. This means that except for the placement of the chapter discussing alicyclic compounds in a better strategic position from the pedagogical standpoint, no fundamental changes have been made. Painstaking revision and addition of material have brought the text thoroughly up to date. The theoretical treatment presenting the compounds of carbon as an integral part of the general science of chemistry, and not as a more or less remotely related branch of this science, constitutes the soul of the book, and remains unchanged. The electronic and other modern theories introduced to show this relation are very adroitly associated with previously accepted theories as if tactfully to indicate advisability, if not absolute necessity, of their adoption. In other words, newer theories are given ample opportunity to edge the older ones out of the science. The general picture of the state and progress of industrial application of organic chemistry is a very satisfactory feature of the book. The publishers have done their part in making the book attractive and durable.

C. E. BOLSER

**Nucleic Acids.** By P. A. LEVENE, The Rockefeller Institute for Medical Research, and LAWRENCE W. BASS, Assistant Director of Research, The Borden Company. American Chemical Society Monograph. The Chemical Catalog Company, Inc., 419 Fourth Ave., New York, 1931. 337 pp. 14 figs. 15.5 × 23.5 cm. Price, $4.50.

This book, the 56th in the series of monographs of the American Chemical Society, takes rank as an authoritative and concise survey of our present knowledge of nucleic acids, to which the senior author, through his own investigations, has contributed so large a share.

The great importance of nucleic acids and their components as constituents of the living cell further contributes toward making this monograph indispensable, not only to the biochemist, biologist, physiologist and physician, but to all who may be interested in synthetic work, structure

and analytical methods in the fields of purine, pyrimidine and sugar chemistry.

The detailed methods given for the separation and preparation of the most important compounds discussed, together with their chemical and physical properties, contribute greatly to the value of this volume to the teacher and investigator interested in organic chemistry and biochemistry.

The monograph, containing eleven chapters, is divided into two parts. Part I, including seven chapters, deals with the components of the nucleic acids. In Part II, the nucleic acids themselves are taken up. The discussion of sugars in Chapter I deals only with their most essential features, "Inasmuch as the present state of sugar chemistry has been reviewed in detail in several monographs." Imidines, imido esters and imidazoles are considered in Chapter II only in so far as they facilitate the understanding of the reactions of the purines. In Chapters III and V are discussed the pyrimidines and purine bases which occur in nucleic acids. The individual compounds are discussed from the standpoint of their discovery, and the historical development of their chemistry and structure. A description of their physical and chemical properties and detailed methods for their separation and preparation, identification and quantitative determination are also given. Chapter IV contains a historical account of the development of uric acid chemistry. Because of the significance of the nucleosides, those groups containing sugar in glucosidic union with nuclein bases, in the development of the structure of nucleic acids, sixty pages in Chapter VI are devoted to the historical development of the structure of the naturally occurring purine and pyrimidine nucleosides. The descriptive part of this chapter deals with the separation of the various nucleosides obtained from nucleic acids, their chemical and physical properties, and their derivatives. A large number of synthetic nucleosides are briefly described. The nucleotides, which are phosphoric esters of the nucleosides, are discussed in Chapter VII. The individual members of this class, including inosinic acid, adenylic acid, guanylic acid, xanthylic acid, and also the pyrimidine nucleotides, together with a number of synthetic nucleotides, are considered from the standpoint of their preparation and properties, rates of hydrolysis and dissociation constants.

In Part II of the monograph is given an account of the discovery of nucleic acids and of their components, a discussion of the structure of nucleic acids, and detailed methods for their preparation with a short chapter on nucleic acids of higher order. The final chapter is devoted to an account of the results of recent investigations on the enzymes, nucleinase, nucleotidase and nucleosidases.

In addition to the text the monograph contains a comprehensive and well arranged author and subject index.

D. BREESE JONES

# BOOKS RECEIVED

January 15, 1932–February 15, 1932

E. H. ARCHIBALD. "The Preparation of Pure Inorganic Substances." John Wiley and Sons, Inc., 440 Fourth Ave., New York. 383 pp. $3.75.

E. F. ARMSTRONG AND K. F. ARMSTRONG. "The Glycosides." Longmans, Green and Company, 55 Fifth Ave., New York. 123 pp. $4.25.

A. BERTHOUD. "Matière et Atomes." Second edition. G. Doin et Cie., 8 Place de l'Odéon, Paris, France. 324 pp. 26 fr.

EARLE RADCLIFFE CALEY. "Analytical Factors and Their Logarithms." John Wiley and Sons, Inc., 440 Fourth Ave., New York. 112 pp. $2.00.

O. ECKSTEIN, A. JACOB AND F. ALTEN. "Arbeiten über Kalidüngen." Verlagsgesellschaft für Ackerbau m. b. H., Schöneberger Strasse 5, Berlin SW 11, Germany. 237 pp. RM. 6.

HERBERT FREUNDLICH. "Kapillarchemie." Vol. II. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 956 pp. M. 60; bound, M. 69.

G. v. HEVESY AND F. PANETH. "Lehrbuch der Radioaktivität." Second edition. Johann Ambrosius Barth Verlag, Salomonstrasse 18B, Leipzig C 1, Germany. 287 pp. RM. 22; bound, RM. 24.

LOUIS S. KASSEL. "The Kinetics of Homogeneous Gas Reactions." American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Ave., New York. 330 pp. $6.50.

R. M. MANLEY. "Kinetic Space and its Consequences." Privately printed by R. M. Manley, 738 Schofield St., Cleveland, Ohio. 93 pp.

JOSEPH NEEDHAM. "Chemical Embryology." Three volumes. The Macmillan Company, 60 Fifth Ave., New York. 2021 pp. $35.00.

F. F. NORD AND R. WEIDENHAGEN, Editors. "Ergebnisse der Enzymforschung." Vol. I. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 377 pp. M. 27; bound, M. 29.

C. UPTHEGROVE AND A. J. HERZIG. "The Effects of the Products of Combustion on the Shrinkage of Metal in the Brass Industry." Bulletin No. 22. Department of Engineering Research, University of Michigan, Ann Arbor, Michigan. 64 pp. $1.00.

"Gmelins Handbuch der anorganischen Chemie." Edited by R. J. MEYER. Eighth edition. System-Number 7, Bromine. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 342 pp. Mk. 56; Mk. 49 to subscribers.

# The Journal of the American Chemical Society

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## SECOND REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY


BY G. P. BAXTER (*Chairman*), MME. M. CURIE, O. HÖNIGSCHMID, P. LE BEAU AND R. J. MEYER


The following report of the Committee covers all atomic weight investigations published in the period February–October, 1931, which have come to its attention. Future reports will cover a twelve-month period.

On the basis of this report, the following changes in the table of atomic weights are recommended: Kr 83.7 instead of 82.9, and Xe 131.3 instead of 130.2.

The determinations are divided according to methods used into the following three classes: (1) physico-chemical methods, (2) chemical methods and (3) physical methods (mass-spectroscopy). Within each class the arrangement of the elements follows the grouping of the periodic system.

Authors of papers bearing on the subject are requested to send copies to each of the five members of the committee at the earliest possible moment.[1]

### I. Physico-Chemical Methods

**Nitrogen.**—T. Batuecas[2] has carried out a new determination of the normal density of nitrous oxide. The gas was prepared by two methods, (1) by the reaction of hydroxylamine hydrochloride and sodium nitrite and (2) by thermal decomposition of ammonium nitrate. It was washed with concentrated sodium hydroxide, pure sulfuric acid and ferrous sulfate solution, dried with solid potassium hydroxide and phosphorus pentoxide, finally condensed with liquid air and subjected to repeated fractionation. Two globes of 1007.55 ml. (G) and 772.58 ml. (3) were employed.

In the following table $P_0$ represents the difference between the pressures

[1] Prof. G. P. Baxter, Coolidge Laboratory, Harvard University, Cambridge, Mass., U. S. A.; Mme. Prof. P. Curie, Institut du Radium, 1, Rue Pierre Curie, Paris V^e^, France; Prof. O. Hönigschmid, Arcisstrasse 1, Munich, Germany; Prof. P. Le Beau, Faculté de Pharmacie, 4 Avenue de l'Observatoire, Paris VI^e^, France; Prof. R. J. Meyer, Meinekestrasse 8, Berlin W. 15, Germany.

[2] Batuecas, *Z. physik. Chem.*, Bodenstein-Festband, 18 (1931).

when filled and exhausted, $S$ the weight of gas, $L_b$ the density calculated according to the formula for a perfect gas and $L_0$ the normal density.

| Series | Globe | $P_0$ | $S$ | $L_b$ | $L_0$ | Mean |
|---|---|---|---|---|---|---|
| 1 | G | 758.13 | 1.98971 | 1.9797 | 1.9809 | 1.9808 |
| | No. 3 | | 1.52559 | 1.9795 | 1.9807 | |
| 2 | G | 773.92 | 2.02945 | 1.9795 | 1.9807 | 1.9807 |
| | No. 3 | | 1.55636 | 1.9796 | 1.9807 | |
| 3 | G | 745.16 | 1.95396 | 1.9779 | 1.9794 | 1.9800 |
| | No. 3 | 744.99 | 1.49890 | 1.9792 | 1.9806 | |
| 4 | G | 761.95 | 1.99977 | 1.9797 | 1.9808 | 1.9807 |
| | No. 3 | | 1.53328 | 1.9795 | 1.9806 | |
| 5 | G | 745.52 | 1.95562 | 1.9787 | 1.9801 | 1.9800 |
| | No. 3 | | 1.49952 | 1.9786 | 1.9800 | |
| 6 | G | 732.34 | 1.92070 | 1.9783 | 1.9800 | 1.9802 |
| | No. 3 | | 1.47311 | 1.9788 | 1.9804 | |
| 7 | G | 752.04 | 1.97243 | 1.9784 | 1.9797 | 1.9799 |
| | No. 3 | | 1.51288 | 1.9788 | 1.9801 | |
| 8 | G | 762.41 | 2.00081 | 1.9795 | 1.9806 | 1.9807 |
| | No. 3 | | 1.53433 | 1.9797 | 1.9808 | |
| 9 | G | 768.33 | 2.01653 | 1.9797 | 1.9807 | 1.9809 |
| | No. 3 | | 1.54653 | 1.9801 | 1.9810 | |
| 10 | G | 752.73 | 1.97498 | 1.9791 | 1.9804 | 1.9803 |
| | No. 3 | | 1.51433 | 1.9790 | 1.9803 | |

The mean[3] of these twenty determinations is found to be 1.98042 ± 0.00005.

Density determinations at $^2/_3$, $^1/_2$ and $^1/_4$ atmospheres are under way from which the value of $1 + \lambda$ will be found.

**Carbon and Sulfur.**—D. LeB. Cooper and O. Maass[4] have determined the density of carbon dioxide at five different temperatures between −30 and 77° over a pressure range of 760 to 250 mm. by filling a globe (5-liter) of known volume at a known temperature and pressure, and, after condensation of the gas in a Pyrex capsule which was sealed by fusion, weighing the condensed gas. The isotherms obtained by plotting molecular weights calculated according to the gas law against the pressure were straight lines whose equations were found by weighing the individual points. Extrapolation to zero pressure yielded the following values for the molecular weight of carbon dioxide and the atomic weight of carbon.

| Degrees | Mol. wt. $CO_2$ | At. wt. C |
|---|---|---|
| 25 | 44.0083 | 12.0083 |
| 0 | 44.0001 | 12.0001 |
| −30 | 44.0079 | 12.0079 |
| Mean | 44.0054 | 12.0054 |

[3] Incorrect in the original: 1.98038.

[4] Cooper and Maass, *Can. J. Res.*, **4**, 283, 495 (1931).

By similar measurements with sulfur dioxide the same authors determined the molecular weight of sulfur dioxide and the atomic weight of sulfur.

| Degrees | Mol. wt. $SO_2$ | At. wt. S |
|---|---|---|
| 0 | 64.064 | 32.064 |
| 25.28 | 64.054 | 32.054 |
| Mean | 64.059 | 32.059 |

No correction for adsorption is applied in either investigation.

**Fluorine.**—H. S. Patterson, R. Whytlaw-Gray and W. Cawood[5] have repeated the work of Moles and Batuecas[6] on the determination of the limiting density of methyl fluoride. The former are of the opinion that methyl fluoride is very difficult to prepare in a state of high purity by the method employed by Moles, and that the density determinations of Moles and Batuecas show variations far larger than the permissible experimental error.

They prepared methyl fluoride according to the method of Collie by thermal decomposition of tetramethylammonium fluoride and purified the gas by liquefaction and repeated fractional distillation. With the aid of the same microbalance which had been employed for the determination of the density of xenon (see below), the equilibrium pressures of oxygen and methyl fluoride corresponding to two different densities were compared. For oxygen pressures of 335.61 and 156.86 mm. at 21° the relative values were 1.06726 and 1.06550, respectively.

By extrapolation to zero pressure the limiting value 1.06395 was found and from this the molecular weight of methyl fluoride, 34.046. Upon the assumption that the atomic weight of carbon is 12.010, a value which they derive from limiting density measurements with highly purified ethylene, they calculate the atomic weight of fluorine to be 19.013. From these results they also calculate the compressibility coefficient at 21° to be 1.00823 and the corresponding value at 0° to be 1.0109 if the thermal expansion coefficient of methyl fluoride is assumed to be a little higher than that of carbon dioxide, an assumption which appears justifiable to the authors. This value is far lower than that calculated by Moles, 1.0180. They believe that his methyl fluoride was contaminated with several per cent. of ether, that therefore his values for the density and the compressibility coefficient are too high, and that only by compensation of errors was the atomic weight 19.000 obtained, corresponding to the finding of the mass spectroscope. They believe it probable that the true atomic weight of fluorine lies nearer 19.010 than 19.000. This points to a slight admixture of a higher isotope although Aston believes fluorine to be a simple element.

[5] Patterson, Whytlaw-Gray and Cawood, *Nature*, **128**, 375 (1931).

[6] Moles and Batuecas, *J. chim. phys.*, **18**, 353 (1920).

**Krypton.**—H. E. Watson[7] has compared the densities of especially pure krypton and oxygen with the aid of a microbalance and finds that the two gases have the same densities at 25° and pressures of 301.15 and 787.8 mm., respectively. On the assumption that proportionality obtains between the compressibility corrections of the two gases, he calculates the atomic weight of krypton to be 83.71, while the most probable value for the compressibility of krypton calculated by him in 1910 yields the value 83.63.

This value while preliminary makes it probable that Aston's value for krypton, 83.77, is nearer the truth than the international value in use up to now, 82.9. Therefore the value 83.7 has been adopted for the table.

**Xenon.**—R. Whytlaw-Gray, H. S. Patterson and W. Cawood[8] with the aid of a highly sensitive microbalance have compared the pressures at which pure xenon provided by F. W. Aston and pure oxygen possess the same densities. The already pure gas was further fractionated until no further increase in density could be detected. For pressures of xenon of 80 and 153 mm. at 18° the relation $P_{O_2}/P_{Xe}$ after applying all corrections was found to be 4.1035 and 4.1049, respectively, as averages of two concordant series. The limiting value of this relation at zero pressure was found by extrapolation to be 4.1020. The atomic weight of xenon is then $4.1020 \times 32 = 131.26$ with an apparent error of $\pm 0.005$. This value corroborates Aston's value, 131.27.

The Committee adopts Xe 131.3 for the table in place of the value heretofore in use.

## II. Chemical Methods

**Nitrogen and Silver.**—G. P. Baxter and C. H. Greene[9] have determined gravimetrically the ratio $Ag:NH_3$. This ratio combined with the ratio $NO_3:Ag$, which has already been determined with a high degree of accuracy, yields the ratio $NO_3:NH_3$, from which the atomic weight of nitrogen referred to oxygen and hydrogen may be calculated.

The method, which has previously been employed by Stas, was as follows. A weighed amount of the purest ammonia, adsorbed on dehydrated and degassed chabazite, was allowed to evaporate into dilute hydrochloric or hydrobromic acid and until the acid was exactly neutralized, with the use of methyl red or litmus as indicator. The ammonium halide was then compared with the purest silver in the usual way with the help of a nephelometer.

All reagents were purified by standard methods. Commercial synthetic liquid ammonia was freed from the more probable impurities such as moisture and uncondensable gases by repeated fractional distillation and

[7] Watson, *Nature*, **127**, 631 (1931).

[8] Whytlaw-Gray, Patterson and Cawood, *ibid.*, **127**, 970 (1931).

[9] Baxter and Greene, THIS JOURNAL, **53**, 604 (1931).

finally was adsorbed in a special weighing tube on chabazite. Actually it is not possible to free ammonia from last traces of moisture in this way, so that in a special series of experiments the percentage of moisture was determined by absorption in fused potassium hydroxide, and a corresponding correction was applied in each experiment.

In the following table the ratio $NO_3$:$NH_3$ is calculated on the assumption that $NO_3$:Ag = 0.57479. The bromide analyses gave in general higher results for the atomic weight of nitrogen than the chloride analyses, apparently owing to occlusion of soluble bromide, and this difference was greater, the higher the concentration of the bromide solution used.

THE ATOMIC WEIGHT OF NITROGEN

| No. | Concn./$n$ | Acid | $NH_3$ in vac. | Ag in vac. | Ag:$NH_3$ | $NO_3$:$NH_3$ | At. wt. N |
|---|---|---|---|---|---|---|---|
| 1 | 0.09 | HCl | 1.43953 | 9.11867 | 6.33448 | 3.64100 | 14.0067 |
| 2 | .07 | HBr | 4.67035 | 29.58295 | 6.33420 | 3.64083 | 14.0078 |
| 3 | .06 | HCl | 4.11520 | 26.06744 | 6.33443 | 3.64097 | 14.0069 |
| 4 | .08 | HBr | 1.62620 | 10.30014 | 6.33387 | 3.64065 | 14.0090 |
| 5 | .15 | HBr | 1.85833 | 11.77004 | 6.33367 | 3.64053 | 14.0098 |
| 6 | .09 | HBr | 1.81372 | 11.48804 | 6.33397 | 3.64070 | 14.0087 |
| 7 | .08 | HCl | 1.61251 | 10.21397 | 6.33421 | 3.64084 | 14.0078 |
| 8 | .03 | HBr | 1.92927 | 12.22037 | 6.33419 | 3.64083 | 14.0078 |
| 9 | .02 | HCl | 1.20999 | 7.66426 | 6.33415 | 3.64081 | 14.0080 |
| 10 | .025 | HBr | 1.67684 | 10.62158 | 6.33428 | 3.64088 | 14.0075 |
| 11 | .03 | HBr | 1.89941 | 12.03092 | 6.33403 | 3.64074 | 14.0084 |
| 12 | .03 | HBr | 1.98867 | 12.59593 | 6.33385 | 3.64063 | 14.0091 |
| | | | Average of chlorides (1, 3, 7, 9) | | | | 14.0074 |
| | | | Average of concentrated bromides (2, 4, 5, 6) | | | | 14.0088 |
| | | | Average of dilute bromides (8, 10, 11, 12) | | | | 14.0082 |
| | | | Average of analyses 1, 3, 7, 8, 9, 10, 11, 12 | | | | 14.0078 |

If the experiments in which the more concentrated bromide solutions were used are omitted, the remaining bromide and chloride analyses yield an atomic weight of nitrogen in excellent agreement with the present international value.

If N = 14.0078, then Ag = 107.879, while if N = 14.008, silver becomes 107.880 from the ratio Ag:$NH_3$ and 107.879 from the ratio Ag:$NO_3$.

**Chlorine.**—Since Scott and Johnson[10] have called attention to an erroneous assumption by O. Hönigschmid and Bedr Chan as to the solubility of silver chloride in water at 0°, Hönigschmid[11] has redetermined this value and finds one in close agreement with that obtained by T. W. Richards and H. H. Willard,[12] *i. e.*, 0.5 mg./liter. Using this value O. Hönigschmid corrects the gravimetric results of the complete silver chloride syntheses of O. Hönigschmid and Bedr Chan.[13]

[10] Scott and Johnson, THIS JOURNAL, **52**, 3586 (1930).

[11] Hönigschmid, *ibid.*, **53**, 3012 (1931).

[12] T. W. Richards and Willard, *ibid.*, **32**, 4 (1910).

[13] Hönigschmid and Chan, *Z. anorg. allgem. Chem.*, **163**, 315 (1927).

In the following table are given the weights of chlorine and silver used, the corrected weight of silver chloride found, the difference between the sum of the chlorine and silver and the silver chloride, and the calculated atomic weight of chlorine.

ATOMIC WEIGHT OF CHLORINE

| No. | Cl in vac. | Ag in vac. | AgCl in vac. | Diff. | Cl:AgCl | At. wt. of Cl |
|---|---|---|---|---|---|---|
| 1 | 2.85458 | 8.68543 | 11.54010 | −0.09 | 0.2473618 | 35.4558 |
| 2 | 2.25569 | 6.86312 | 9.11889 | − .08 | .2473645 | 35.4563 |
| 4 | 2.46049 | 7.48635 | 9.94704 | − .20 | .2473590 | 35.4553 |
| 5 | 3.35955 | 10.22139 | 13.58106 | − .12 | .2473702 | 35.4574 |
| 6 | 2.96007 | 9.00620 | 11.96637 | − .10 | .2473657 | 35.4565 |
| 7 | 2.21357 | 6.73502 | 8.94863 | − .04 | .2473641 | 35.4562 |
| 8 | 3.04333 | 9.25949 | 12.30290 | − .08 | .2473669 | 35.4568 |
| 9 | 2.17711 | 6.62409 | 8.80133 | − .13 | .2473615 | 35.4558 |
| | 21.32439 | 64.88109 | 86.20632 | − .84 | .2473646 | 35.4563 |

The mean atomic weight of chlorine from these eight gravimetric determinations is 35.4563 while by nephelometric titration 35.4567 was found. The average deviation between the weights of silver chloride calculated and found is 0.1 mg. and the total for eight determinations is 0.84 mg.

**Iodine.**—G. P. Baxter and A. Q. Butler[14] have again undertaken the investigation of iodine pentoxide, begun more than twenty years ago by Baxter and Tilley[15] in order to explain the discrepancy between the ratio $2Ag:I_2O_5$ as determined experimentally, 0.646225, and that calculated from the atomic weights Ag = 107.880 and I = 126.932, 0.646251. A small part of this difference is explained by the discovery that air is adsorbed by the very porous iodine pentoxide to the extent of 0.001%.

Analysis was carried out by thermal decomposition of weighed amounts of the pentoxide and weighing of the iodine liberated.

Iodic acid was obtained by metathesis from sulfuric acid and barium iodate, which had been prepared from pure materials, and was purified by fractional crystallization. The acid was dehydrated at gradually increasing temperatures (100–240°). The decomposition was conducted in a special quartz weighing tube, which could be closed with ground stoppers, in which the resulting iodine was condensed for weighing. Since the pentoxide cannot be entirely freed from moisture at the highest temperature at which it is stable, in each analysis a water determination was made by passing the oxygen evolved through a weighed U-tube containing phosphorus pentoxide. The water determinations were subject to a blank correction obtained in a special series of experiments. In addition a correction was made of 0.001% for air adsorbed on the pentoxide.

[14] Baxter and Butler, THIS JOURNAL, **53**, 968 (1931).

[15] Baxter and Tilley, *ibid.*, **31**, 201 (1909).

THE RATIO OF IODINE TO IODINE PENTOXIDE

| No. | Corr. wt. of $I_2O_5$ | I in vac. | O in vac. | $I_2:I_2O_5$ | $I_2:5O$ |
|---|---|---|---|---|---|
| 1 | 23.43527 | 17.81810 | 5.61717 | 0.760311 | 3.17208 |
| 2 | 25.52824 | 19.40949 | 6.11875 | .760314 | 3.17213 |
| 3 | 42.45905 | 32.28337 | 10.17568 | .760341 | 3.17260 |
| 4 | 46.13308 | 35.07699 | 11.05609 | .760344 | 3.17264 |
| 5 | 46.22581 | 35.14741 | 11.07840 | .760342 | 3.17261 |
| 6 | 21.05562 | 16.00913 | 5.04649 | .760326 | 3.17233 |
| 7 | 22.07654 | 16.78564 | 5.29090 | .760338 | 3.17255 |
| 8 | 41.88974 | 31.85032 | 10.03942 | .760337 | 3.17253 |
| 9 | 42.71266 | 32.47602 | 10.23664 | .760337 | 3.17253 |
| | | | Average | .760332 | 3.17244 |
| | | | Average 3, 4, 5, 7, 8, 9 | .760340 | 3.17259 |

Analyses 1, 2 and 6 were rejected since they were subject to known errors. The values for the ratio of iodine to oxygen and to pentoxide are subject to a correction for displacement of air from the weighing tube by iodine vapor at 25°. The effect of this is to raise the value of the ratio $I_2:5O$ by 0.001% to 3.17262 and of the ratio $I_2:I_2O_5$ by 0.0003% to 0.760342.

The result of these analyses is very surprising since the values for these ratios calculated from the atomic weight of iodine, 126.932, are 3.17330 and 0.760381, respectively. The atomic weight of iodine calculated from the analytical data is 126.905. Since this value is believed to be impossibly low, the conclusion is reached that the most carefully prepared iodine pentoxide contains more oxygen than corresponds to its stoichiometric composition, apparently because of the presence of a higher oxide of iodine, and that it is therefore unsuited as a starting point for experiments of high precision. This conclusion is supported by the result of the earlier investigation by Baxter and Tilley in which the ratio $2Ag:I_2O_5$ was found to be smaller than that expected. By combination of the experimentally determined ratios, $2Ag:I_2O_5$ and $I_2:I_2O_5$ the ratio I:Ag may be calculated to be 1.176579 and the atomic weight of iodine 126.929.

O. Hönigschmid and H. Striebel[16] have completed an investigation on the atomic weight of iodine by determining the ratio AgI:AgCl. The silver iodide was obtained by synthesis from the purest atomic weight silver and carefully purified iodine The purification of the iodine followed the procedure recommended by Guichard, and consisted essentially in decomposing potassium iodide with copper sulfate and purifying the iodine which separated by distillation from solution in potassium iodide and sublimation. The silver iodide, contained in a weighed quartz tube, was fused in an atmosphere containing iodine vapor and after being weighed was converted to chloride by heating in a current of chlorine. All weighings were made by substitution with the use of counterpoises and were corrected to vacuum.

[16] Hönigschmid and Striebel, *Z. physik. Chem.*, Bodenstein-Festband, 282 (1931).

THE RATIO OF SILVER IODIDE TO SILVER CHLORIDE

| No. | AgI in vac. | AgCl in vac. | AgI:AgCl | At. wt. I |
|---|---|---|---|---|
| 1 | 4.07537 | 2.48790 | 1.638076 | 126.917 |
| 2 | 5.41399 | 3.30511 | 1.638067 | 126.916 |
| 3 | 6.45241 | 3.93901 | 1.638079 | 126.917 |
| 4 | 7.20017 | 4.39557 | 1.638051 | 126.913 |
| 5 | 6.74801 | 4.11943 | 1.638093 | 126.919 |
| 6 | 8.42163 | 5.14113 | 1.638078 | 126.917 |
| 7 | 8.79602 | 5.36972 | 1.638078 | 126.917 |
| | 47.10760 | 28.75787 | 1.638076 | 126.917 |

These seven concordant determinations yield for the atomic weight of iodine the strikingly low value 126.917 if chlorine is assumed to have the value 35.457.

The authors call attention to the fact that on the basis of Aston's value for the atomic weight of iodine based on $O_{16} = 16$, 126.932, the chemical atomic weight must be about 1/10000 lower, not far from 126.918, providing always that the relation $A_{mass.} = A_{chem.} \times 1.000125$, which depends on Babcock and Naudé's determination of the isotopic proportion $O_{16}:O_{18}:O_{17}$, is correct. From a similar determination by Mecke and Childs the relation $A_{mass.} = A_{chem.} \times 1.00022$ has been obtained, and from Aston's value for iodine the chemical value 126.905, which is identical with that calculated from Baxter and Butler's data already given. However, Aston's value is a mean of the observed limiting values 126.907 and 126.957 so that aside from the uncertainty of the conversion factor, calculations of this kind will have no definite significance until the accuracy of the mass spectrographic measurements is increased.

## III. Physical Methods

In continuation of his investigations with the mass spectrograph, F. W. Aston[17] has calculated the chemical atomic weights of several elements from the results of microphotometric measurements of the intensities of isotopic lines. For conversion from the physical basis $O_{16} = 16.000$ to the chemical basis $O = 16.000$, Naudé's equation is used. $O_{chem.}:O_{16} = 1.000125:1.000000$.

**Oxygen.**—R. Mecke and W. H. J. Childs[18] have completed a new determination of the relative proportions of the oxygen isotopes by microphotometric evaluation of the band spectrum of oxygen, with the following result: $O_{16}:O_{18}:O_{17} = 630 \pm 20:1:0.2$. On the basis of $O_{16} = 16$ the atomic weight of chemical oxygen is calculated to be $16.0035 \pm 0.0003$. The conversion of atomic weights determined with the mass spectroscope to

[17] Aston, *Nature*, **127**, 233, 519, 813; **128**, 149 (1931); *Proc. Roy. Soc.*, **A132**, 487 (1931).

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

## Atomic Weights

1932

| | Symbol | Atomic Number | Atomic Weight |
|---|---|---|---|
| Aluminum | Al | 13 | 26.97 |
| Antimony | Sb | 51 | 121.76 |
| Argon | A | 18 | 39.944 |
| Arsenic | As | 33 | 74.93 |
| Barium | Ba | 56 | 137.36 |
| Beryllium | Be | 4 | 9.02 |
| Bismuth | Bi | 83 | 209.00 |
| Boron | B | 5 | 10.82 |
| Bromine | Br | 35 | 79.916 |
| Cadium | Cd | 48 | 112.41 |
| Calcium | Ca | 20 | 40.08 |
| Carbon | C | 6 | 12.00 |
| Cerium | Ce | 58 | 140.13 |
| Cesium | Cs | 55 | 132.81 |
| Chlorine | Cl | 17 | 35.457 |
| Chromium | Cr | 24 | 52.01 |
| Cobalt | Co | 27 | 58.94 |
| Columbium | Cb | 41 | 93.3 |
| Copper | Cu | 29 | 63.57 |
| Dysprosium | Dy | 66 | 162.46 |
| Erbium | Er | 68 | 167.64 |
| Europium | Eu | 63 | 152.0 |
| Fluorine | F | 9 | 19.00 |
| Gadolinium | Gd | 64 | 157.3 |
| Gallium | Ga | 31 | 69.72 |
| Germanium | Ge | 32 | 72.60 |
| Gold | Au | 79 | 197.2 |
| Hafnium | Hf | 72 | 178.6 |
| Helium | He | 2 | 4.002 |
| Holmium | Ho | 67 | 163.5 |
| Hydrogen | H | 1 | 1.0078 |
| Indium | In | 49 | 114.8 |
| Iodine | I | 53 | 126.932 |
| Iridium | Ir | 77 | 193.1 |
| Iron | Fe | 26 | 55.84 |
| Krypton | Kr | 36 | 83.7 |
| Lanthanum | La | 57 | 138.90 |
| Lead | Pb | 82 | 207.22 |
| Lithium | Li | 3 | 6.940 |
| Lutecium | Lu | 71 | 175.0 |
| Magnesium | Mg | 12 | 24.32 |
| Manganese | Mn | 25 | 54.93 |
| Mercury | Hg | 80 | 200.61 |
| Molybdenum | Mo | 42 | 96.0 |
| Neodymium | Nd | 60 | 144.27 |
| Neon | Ne | 10 | 20.183 |
| Nickel | Ni | 28 | 58.69 |
| Nitrogen | N | 7 | 14.008 |
| Osmium | Os | 76 | 190.8 |
| Oxygen | O | 8 | 16.0000 |
| Palladium | Pd | 46 | 106.7 |
| Phosphorus | P | 15 | 31.02 |
| Platinum | Pt | 78 | 195.23 |
| Potassium | K | 19 | 39.10 |
| Praseodymium | Pr | 59 | 140.92 |
| Radium | Ra | 88 | 225.97 |
| Radon | Rn | 86 | 222 |
| Rhenium | Re | 75 | 186.31 |
| Rhodium | Rh | 45 | 102.91 |
| Rubidium | Rb | 37 | 85.44 |
| Ruthenium | Ru | 44 | 101.7 |
| Samarium | Sm | 62 | 150.43 |
| Scandium | Sc | 21 | 45.10 |
| Selenium | Se | 34 | 79.2 |
| Silicon | Si | 14 | 28.06 |
| Silver | Ag | 47 | 107.880 |
| Sodium | Na | 11 | 22.997 |
| Strontium | Sr | 38 | 87.63 |
| Sulfur | S | 16 | 32.06 |
| Tantalum | Ta | 73 | 181.4 |
| Tellurium | Te | 52 | 127.5 |
| Terbium | Tb | 65 | 159.2 |
| Thallium | Tl | 81 | 204.39 |
| Thorium | Th | 90 | 232.12 |
| Thulium | Tm | 69 | 169.4 |
| Tin | Sn | 50 | 118.70 |
| Titanium | Ti | 22 | 47.90 |
| Tungsten | W | 74 | 184.0 |
| Uranium | U | 92 | 238.14 |
| Vanadium | V | 23 | 50.95 |
| Xenon | Xe | 54 | 131.3 |
| Ytterbium | Yb | 70 | 173.5 |
| Yttrium | Y | 39 | 88.92 |
| Zinc | Zn | 30 | 65.38 |
| Zirconium | Zr | 40 | 91.22 |

| | Isotopic weights and percentages | | | | | | | | Packing fraction | Atomic weight |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | O = 16 |
| Lithium | 6 | 7 | | | | | | | $+20 \times 10^{-4}$<br>$+17 \times 10^{-4}$ | 6.923 |
| | 8.9 | 91.1 | | | | | | | | |
| Cesium | 133 | | | | | | | | $-5 \times 10^{-4}$ | 132.91 |
| | 100 | | | | | | | | | |
| Boron | 10 | 11 | | | | | | | $+13.5 \times 10^{-4}$<br>$+10.0 \times 10^{-4}$ | 10.806 |
| | 20.7 | 79.3 | | | | | | | | |
| Germanium | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | between $-7$ and $-10 \times 10^{-4}$ | 72.65 |
| | 19.72 | 1.53 | 25.41 | 9.22 | 35.47 | 2.26 | 6.09 | 0.70 | | |
| Selenium | 74 | 76 | 77 | 78 | 80 | 82 | | | $-7.3 \times 10^{-4}$ | 78.96 |
| | 0.9 | 9.5 | 8.3 | 24.0 | 48.0 | 9.3 | | | | |
| Tellurium | 125 | 126 | 128 | 130 | | | | | $-5 \times 10^{-4}$ | 128.03 |
| | 6.6 | 20.9 | 36.1 | 36.4 | | | | | | |
| Tungsten | 182 | 183 | 184 | 186 | | | | | 0 | 183.96 |
| | 22.6 | 17.2 | 30.1 | 30.0 | | | | | | |
| Bromine | 79 | 81 | | | | | | | $-9.0 \times 10^{-4}$<br>$-8.6 \times 10^{-4}$ | 79.916 |
| | 50 | 50 | | | | | | | | |
| Rhenium | 185 | 187 | | | | | | | $-1 \times 10^{-4}$ | 186.22 |
| | 38.2 | 61.8 | | | | | | | | |
| Ruthenium | 96 | 98 | 99 | 100 | 101 | 102 | 104 | | $-6 \times 10^{-4}$ | 101.1 |
| | 5 | | 12 | 14 | 22 | 30 | 17 | | estimated | |
| Osmium | 186 | 187 | 188 | 189 | 190 | 192 | | | $-1 \times 10^{-4}$ | 190.31 |
| | 1.0 | 0.6 | 13.5 | 17.3 | 25.1 | 42.6 | | | | |

the chemical basis would then need to follow the equation $A_{\text{mass.}} = A_{\text{chem.}} \times 1.00022$ while at present the Naudé conversion factor 1.000125 is in use.

**The Atomic Weight Standard.**—The discovery of the oxygen isotopes has created the undesirable situation that chemistry and physics are using two different scales for the determination of atomic weights. Because of this the question of an absolute standard has already been more or less widely discussed and various proposals made, for instance, $H_1 = 1.00000$; $He_4 = 4.00000$; $O_{16} = 16.0000$ as well as the present chemical standard O = 16.0000.

F. W. Aston, who discussed the question comprehensively before the British Association in 1931, concludes that it is advisable for chemists to retain the present chemical standard, since it amply satisfies all requirements of International Atomic Weights so far as accuracy is concerned. For the more exacting requirements of physics the oxygen isotope $O_{16}$ seems to him a better standard. The disadvantage that the two scales differ by one or two parts in ten thousand and that this difference will be subject to continual revision does not seem particularly important to him. Confusion may be easily avoided by speaking in one case of the "atomic weight for chlorine" and in the other of the "weight of the chlorine atom 35."

The Committee agrees unanimously with Aston's opinion and sees no reason for proposing a change in the present standard of atomic weights, O = 16.0000.

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

# LIQUID JUNCTION POTENTIALS. I. REPRODUCIBLE STATIC LIQUID JUNCTIONS CONSTANT IN POTENTIAL OVER LONG PERIODS OF TIME[1]

BY ALFRED L. FERGUSON, KENNETH VAN LENTE AND RICHARD HITCHENS

RECEIVED JULY 27, 1931 PUBLISHED APRIL 6, 1932

Static liquid junctions have caused endless difficulties since measurements of single electrode and concentration cell potentials were first attempted.[2] To get results at all reproducible, investigators have adopted numerous arbitrary methods for overcoming these difficulties, but none are accepted as satisfactory. Such procedures, of course, have rendered the data empirical.[3] An extensive study of the most promising devices was made by Lamb and Larson.[4] They concluded that results with static junctions, made in various ways, are unsatisfactory, and, therefore, proceeded to develop the flowing junction.

There are many instances, however, where it is not possible or convenient to use flowing junctions and yet it is highly important that constant and reproducible values be obtained; for instance, in the comparison of the standard hydrogen with a calomel or any other electrode, liquid junction potential is included in the measurement and becomes a part of the value given to the calomel or other electrode. All such values are as uncertain as the boundary potential, and whenever the calomel electrode is used as a standard the assumption must be made that the solution potential, which is a part of its value, always remains the same. When a saturated calomel electrode or a bridge of saturated potassium chloride is used, the common assumption is that no boundary potential exists under these conditions. It is well known, however, that neither of these assumptions is justified. The present work is an attempt to construct static boundaries of this nature in such a manner as to give potentials more constant and reproducible than have previously been done. The

[1] The material in this article is from a portion of the thesis submitted to the Graduate School of the University of Michigan by Kenneth Van Lente in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] The present authors do not include a bibliography because several are now in print; see, for instance, Guggenheim, THIS JOURNAL, **52**, 1315 (1930).

[3] These remarks do not apply to junctions which consist of two different concentrations of the same electrolyte. Such boundaries, according to both theory and practice, give but little trouble.

[4] Lamb and Larson, THIS JOURNAL, **42**, 229 (1920).

systems used were selected because of their importance in connection with the determination of the relative values of calomel electrodes and because saturated calomel electrodes, or other calomel electrodes in conjunction with a saturated potassium chloride bridge, are so extensively used in $P_H$ measurements.

Most valuable contributions, both theoretical and experimental, to this field have been made recently by Maclagan, Bjerrum, Guggenheim and their co-workers.[5,2] Some of the systems used by these investigators are similar to those herein described. Unmack and Guggenheim, in their last article on this topic, introduced several improvements upon their earlier works, but still they state the tenth normal calomel electrodes have a probable error of $\pm 0.15$ mv. and the 3.5 normal are "less stable and slightly less reproducible." Concerning the boundary potentials it is stated, "We reduced the erratic fluctuations of the free diffusion measurements from about $\pm 0.25$ mv. to $\pm 0.1$ mv." The saturated calomel electrodes used in the present work showed a maximum variation of 0.05 mv. and remained constant to 0.02 mv. for several months. One of the major factors in this reproducibility and constancy is the maintenance of a constant temperature throughout the whole period. Freshly prepared electrodes required several days in the constant temperature bath before their potentials became stable; and when electrodes were left out of the bath while cells were being reassembled, it required several hours to regain their former value.

## Apparatus and Materials

**Electrodes.**—Several saturated calomel electrodes were used as references. The type was a slight modification of that used by G. N. Lewis.[6] Much care was exercised in their preparation. The silver chloride electrodes were made by a method closely similar to that recommended by Carmody.[7] Such electrodes were fairly reproducible and remained constant to within 0.02 mv. for periods of time longer than the cells were measured.

The liquid junction vessels were 9-mm. three-way stopcocks. The stopcocks were placed in such a position that the junctions were horizontal in vertical tubes (see E, Fig. 2). A special stopcock grease, made by heating at 110° a mixture of equal weights of crepe rubber and white vaseline until it became uniform in body, was found necessary to prevent oil from leaking in and liquid from seeping around the stopcock.

**Measuring Apparatus.**—The potentials were measured on a Leeds and Northrup Type K potentiometer equipped with a Leeds and Northrup 2285-c High Sensitivity galvanometer. The Weston saturated standard cell was calibrated by the Bureau of Standards. Measurements were checked frequently on another potentiometer set-up in the same room and always found to agree within 0.01 mv. The temperature was maintained constant at 25.00° by an electrically controlled oil-bath.

[5] Maclagan, *Biochem. J.*, **23**, 309 (1929); Unmack and Guggenheim, *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **10**, No. 8 (1930).

[6] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

[7] Carmody, *ibid.*, **51**, 2901 (1929).

**Solutions.**—Extensive precautions were taken to make certain that the potassium chloride solutions were at all times saturated. This is an important factor. The hydrochloric acid solutions were made from redistilled Baker and Adamson C. P. hydrochloric acid. They were analyzed by three gravimetric determinations and the results showed that they were exact for this work.

## Experimental

Boundaries were made first in the customary manner by dipping the side arms of two saturated calomel electrodes into a beaker of 0.10 *M*

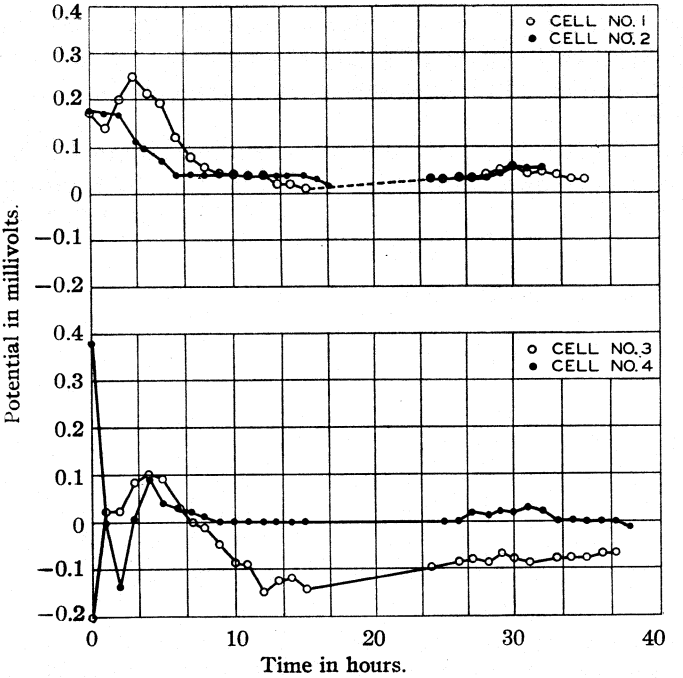


Fig. 1.—Curves showing how the potentials of the cells Hg–HgCl–satd. KCl/0.10 *M* HCl/satd. KCl–HgCl–Hg; Hg–HgCl–satd. KCl/0.01 *M* HCl/satd. KCl–HgCl–Hg varied with time when the junctions were made horizontally in 9-mm. stopcocks.

hydrochloric acid. The potentials were neither zero, reproducible nor constant. The nature of the junction was varied in several ways. The electrode side arms with and without constricted tips in some cases were dipped straight down into the acid solution; in others the tips were turned up, and in still others the vertical parts of the tubes were filled with various mixtures of the two solutions so as to produce a more "continuous mixture" boundary. The results showed clearly that cells which contain liquid junctions between saturated potassium chloride and 0.10 *M* hydrochloric acid solutions made by any of these methods are indefinite to the extent of 0.2 mv. or more.

In earlier work in this Laboratory the major boundary under investigation has been made in three-way stopcocks with considerable success. In the present work this system was applied also to the supporting boundaries which are usually made in an indefinite manner. The two following types of cells were used

Hg–HgCl–satd. KCl / 0.10 *M* HCl / satd. KCl–HgCl–Hg
Hg–HgCl–satd. KCl / 0.01 *M* HCl / satd. KCl–HgCl–Hg

Typical results are represented in Fig. 1. The potentials, of course, should be zero, but, especially at first, this is not the case. The results show, however, that in time the potentials approach zero and remain so for many hours. They are more constant and reproducible than any previously reported.

Boundaries made in this manner were then incorporated into a typical cell involving boundary potential. The cell may be represented as

Hg–HgCl–satd. KCl / 0.01 *M* HCl / 0.10 *M* HCl / satd. KCl–HgCl–Hg
AgCl–Ag AgCl–Ag

A diagram of the set-up is shown in Fig. 2.

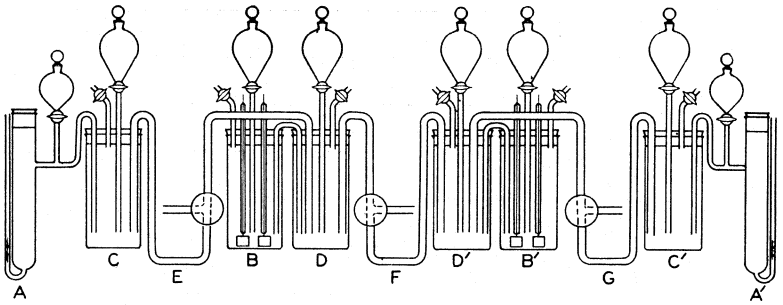


Fig. 2.—A diagram of the apparatus in which were made the cells Hg–HgCl–satd. KCl/0.01*M* HCl/0.10 *M* HCl/satd. KCl–HgCl–Hg.
AgCl–Ag AgCl–Ag

With this arrangement the combined potential of all three boundaries could be determined, and also any variations in individual boundaries.

A typical set of data is given in Table I. The letters above each column correspond to those used to designate the parts of the cell system represented at the head of the table and in Fig. 2, and indicate over what portion of the whole cell system the values in the respective columns apply. The last three columns give data regarding the constancy of the three individual boundaries, G, F, and E, respectively. It is obvious that the individual boundaries are extremely constant in potential. The potential between the two concentrations of hydrochloric acid is as constant as the silver chloride electrodes themselves, which is in complete agreement with past experimental work by many investigators.

TABLE I

A TYPICAL EXAMPLE OF THE RESULTS OBTAINED WITH A CELL OF THE TYPE

Hg–HgCl–satd. KCl / 0.01 *M* HCl / 0.10 *M* HCl / satd. KCl–HgCl–Hg

AgCl–Ag AgCl–Ag

| A | B | B′ | A′ |
|---|---|---|---|
| Time, hours | Pot. A-A′, mv. | Pot. B′-A′, mv. | Pot. B-B′, mv. | Pot. A-B, mv. |
| 0 | 37.99 | 44.81 | 92.37 | 99.19 |
| 1 | 37.97 | 44.79 | 92.37 | 99.19 |
| 2 | 37.95 | 44.76 | 92.37 | 99.18 |
| 3 | 37.95 | 44.75 | 92.38 | 99.18 |
| 4 | 37.93 | 44.73 | 92.38 | 99.18 |
| 5 | 37.92 | 44.73 | 92.38 | 99.19 |
| 6 | 37.93 | 44.75 | 92.38 | 99.20 |
| 7 | 37.92 | 44.76 | 92.37 | 99.21 |
| 8 | 37.93 | 44.77 | 92.37 | 99.21 |
| 9 | 37.93 | 44.78 | 92.37 | 99.22 |
| 10 | 37.92 | 44.77 | 92.38 | 99.22 |
| 11 | 37.93 | 44.77 | 92.37 | 99.21 |
| 12 | 37.94 | 44.77 | 92.37 | 99.20 |
| 13 | 37.94 | 44.77 | 92.37 | 99.20 |
| 14 | 37.94 | 44.77 | 92.38 | 99.20 |
| 15 | 37.98 | 44.77 | 92.37 | 99.17 |
| 24 | 38.07 | 44.76 | 92.36 | 99.06 |
| 25 | 38.09 | 44.76 | 92.37 | 99.06 |
| 26 | 38.09 | 44.76 | 92.36 | 99.05 |
| 27 | 38.07 | 44.76 | 92.37 | 99.06 |
| 28 | 38.07 | 44.76 | 92.37 | 99.07 |
| 29 | 38.00 | 44.76 | 92.37 | 99.14 |
| 30 | 37.96 | 44.76 | 92.37 | 99.17 |
| 31 | 37.93 | 44.76 | 92.37 | 99.21 |
| 32 | 37.93 | 44.76 | 92.38 | 99.21 |
| 33 | 37.97 | 44.76 | 92.37 | 99.17 |
| 34 | 37.98 | 44.76 | 92.37 | 99.16 |
| 35 | 37.99 | 44.76 | 92.38 | 99.15 |
| 36 | 37.98 | 44.76 | 92.37 | 99.15 |
| 37 | 37.99 | 44.77 | 92.37 | 99.15 |
| 38 | 37.99 | 44.77 | 92.38 | 99.15 |
| 48 | 37.99 | 44.77 | 92.38 | 99.15 |
| Av. | 37.98 | 44.76 | 92.37 | 99.16 |
| Av. dev. | ±0.04 | ±0.01 | ±0.00 | ±0.04 |

It should be mentioned that the technique involved in making the assembly is an important factor. After all parts were rigidly located through the use of suitable supports and clamps and the vessels filled with their respective solutions, the boundaries were formed within the large three-way stopcocks. To do this the lower part was filled by suction with the more dense solution, the stopcock was then turned through 180°, the remaining solution drawn out, the stopcock washed several times with

the less dense solution, and finally filled by suction with the less dense solution. It was closed by turning through an angle of 45°. In adjusting the liquid levels, account had to be taken, of course, of the difference in densities of the solutions on opposite sides of the boundary.

The apparatus was left in the thermostat overnight. The next morning the small stopcock in each beaker was opened to ensure atmospheric pressure. The boundaries were then formed by turning the large stopcocks through 45°, and were left undisturbed throughout the experiment. These are true "free diffusion boundaries."

In order to test the reproducibility and constancy over long periods of time of the potentials of this cell system and to establish an accurate value for the so-called boundary potential between 0.1 and 0.01 *N* hydrochloric acid, fifteen cells were measured which were the same as those described above. The results are recorded in Table II. The first column

TABLE II

A SUMMARY OF THE RESULTS OBTAINED WITH FOURTEEN CELLS OF THE TYPE Hg–HgCl–satd. KCl/0.01 *M* HCl/0.10 *M* HCl/satd. KCl–HgCl–Hg

| Time, hours | Av. pot., mv. | Av. dev., mv. |
|---|---|---|
| 26 | 38.08 | ±0.03 |
| 48 | 38.09 | ± .05 |
| 29 | 38.03 | ± .03 |
| 43 | 38.10 | ± .04 |
| 51 | 38.06 | ± .06 |
| 48 | 38.03 | ± .07 |
| 13 | 38.08 | ± .03 |
| 42 | 38.04 | ± .05 |
| 14 | 38.00 | ± .04 |
| 12 | 37.97 | ± .03 |
| 11 | 37.97 | ± .02 |
| 32 | 38.12 | ± .01 |
| 49 | 37.99 | ± .07 |
| 48 | 37.98 | ± .04 |
| | Av. 38.04 | |

gives the number of hours during which readings were made on the respective cells; the second, the average potentials in mv. over the time interval indicated; the third, the averages of the deviations of the single readings from the average of each cell. The average potential of all the averages is 38.04 mv. The maximum deviation of this average potential from that for any one cell is 0.08 mv. and the mean of the average deviations is ±0.04 mv.

## Summary

1. An improved method for making a "free diffusion" type of static junction is described.

2. Static junctions of the type 0.1 *M* HCl/satd. KCl or 0.01 *M* HCl/satd. KCl must be made very definitely in order to be reproducible or constant, and when so made are constant for days to ±0.04 mv. average deviation, and reproducible to less than 0.1 mv.

3. The junction between 0.1 and 0.01 *M* hydrochloric acid is constant and reproducible within the limits of dependability of the silver chloride electrodes used, or within 0.02 mv.

4. The potential of the cell system

Hg–HgCl–satd. KCl/0.01 *M* HCl/0.10 *M* HCl/satd. KCl–HgCl–Hg

commonly called the boundary potential between 0.01 and 0.10 *M* hydrochloric acid has been determined to be 38.04 ± 0.04 mv. average deviation.

ANN ARBOR, MICHIGAN

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

# LIQUID JUNCTION POTENTIALS. II. A DIRECT COMPARISON OF STATIC AND FLOWING JUNCTIONS[1]

BY ALFRED L. FERGUSON, KENNETH VAN LENTE AND RICHARD HITCHENS

RECEIVED JULY 27, 1931 PUBLISHED APRIL 6, 1932

Many careful and extensive investigations during the last quarter century developed the general feeling that static liquid junctions are neither reproducible nor constant. This situation led to the development of the flowing junction.

Lamb and Larson,[2] who were the first to work extensively with the flowing junction, formed their junctions by allowing the more dense solution to flow up a vertical tube and meet the less dense solution flowing down, both then flowed out a common horizontal exit. This junction gave results constant and reproducible to one or two hundredths of a millivolt but the values were different from those which they obtained with static junctions. They also differed as much as 2.46 mv. from results obtained with another type of flowing junction apparatus which they used.

MacInnes and Yeh,[3] with a modified form of the Lamb and Larson apparatus, showed that the potentials of cells containing solutions of the same concentration of a common ion varied with the rate of flow. They showed, also, that the potentials increase appreciably at low rates and decrease slightly at high rates of flow. Scatchard[4] modified the apparatus used by MacInnes and Yeh in order to obtain an equal rate of

[1] The material presented in this article is from a portion of the thesis submitted to the Graduate School of the University of Michigan by Kenneth Van Lente in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Lamb and Larson, THIS JOURNAL, **42**, 229 (1920).

[3] MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

[4] Scatchard, *ibid.*, **47**, 696 (1925).

flow of the solutions. He also lengthened the horizontal part of the outlet tube to lessen the effects of mixing. His results with solutions of hydrochloric acid and saturated potassium chloride were reproducible and constant to a few hundredths mv. even with molal hydrochloric acid. He found that the potentials always rose when the flow was stopped, the maximum rise being 3.5 mv.

Other types of flowing junctions have been used by Aten and Van Dalfsen,[5] by Roberts and Fenwick,[6] and by Maclagan.[7]

It is evident from the literature that for a given piece of apparatus the flowing junction gives reproducible potentials at constant rates of flow but the values differ for different pieces of apparatus, and with the rate of flow, and do not agree with the values for static junctions.

The authors, in an earlier article, have described a method for obtaining highly reproducible and constant potentials for static junctions between saturated potassium chloride and different concentrations of hydrochloric acid. In the present work the apparatus was modified somewhat to make it possible to compare directly the potentials of static and flowing junctions.

## Apparatus

**Stopcock.**—The stopcock which permitted the direct comparison of static and flowing junctions is shown in Fig. 1. A horizontal static junction may be made at the lower edge as described in the previous article. For the best results it is essential that the bore of the stopcock be exactly the same as that of the tubes leading to it. It was found necessary to have these made to order. The rate of flow was controlled by a stopcock in the exit tube. The small projection within the stopcock and opposite the outlet tube prevents the solutions from mixing when the junction is flowing. Preliminary experiments with sodium hydroxide solution on one side and water containing phenolphthalein on the other showed a very thin red ribbon-like layer which extended from the tip of the projection completely throughout the exit tube. This layer indicated that the junction was very thin at medium rates, somewhat mixed at high rates and diffuse at low rates of flow.

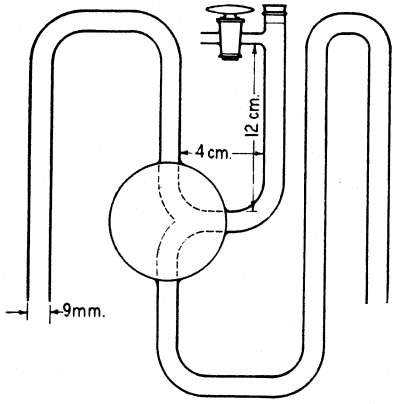


Fig. 1.—A diagram of a 9-mm. three-way stopcock which permitted the direct comparison of static and flowing junctions.

The measuring apparatus is the same as described in the previous article, except that the small dropping funnels were replaced with those of 250-cc. capacity in order to supply sufficient solutions for the flowing junctions, thus making readjustment of the levels of the solutions infrequent.

[5] Aten and Van Dalfsen, *Rec. trav. chim.*, **45**, 177 (1926).

[6] Roberts and Fenwick, THIS JOURNAL, **49**, 2787 (1927).

[7] Maclagan, *Biochem. J.*, **23**, 309 (1929).

## Experimental

The first cell studied was the concentration cell

Ag–AgCl–0.01 *M* HCl / 0.10 *M* HCl–AgCl–Ag

It consisted of two silver chloride electrode vessels with side arms dipping into beakers of the respective acid solutions. These two beakers were joined by one of the large stopcocks shown in Fig. 1, in which the liquid junction was made. The potentials of the static junctions were measured over periods of about twenty-five hours; then the static junctions were changed to flowing. The rate of flow was not changed in any case until the potential had become constant to 0.01 mv. for at least fifteen minutes.

In order to determine how much of the flowing junction was actually effective, the solutions in the outlet tube were stirred with a piece of fine rubber tubing. This stirring was started at the top of the vertical tube and continued until the solutions in the stopcock itself were mixed. The corresponding changes in potential were noted.

A summary of the results obtained with this concentration cell is given in Table I.

TABLE I

A COMPARISON OF THE VALUES OBTAINED WITH A CONCENTRATION CELL USING VARIOUS TYPES OF LIQUID JUNCTIONS

| Cell no. | Static pot., mv. | Flowing pot. Low 0.3 cc. per min. | Flowing pot. Med. 1.0 cc. per min. | Flowing pot. High 2.0 cc. per min. | Stopped flow pot., mv. | Stirred junct. pot., mv. |
|---|---|---|---|---|---|---|
| 1 | 92.27 | 92.32 | 92.32 | 92.30 | 92.30 | 92.30 |
| 2 | ... | 92.33 | 92.33 | 92.30 | ... | ... |
| 3 | 92.27 | 92.32 | 92.30 | 92.30 | 92.30 | 92.30 |
| 4 | ... | 92.32 | 92.30 | 92.31 | 92.30 | 92.30 |

It may be seen from Table I that the type of junction in a concentration cell makes practically no difference in the potential. These results confirm those obtained by Scatchard and Buehrer[8] with somewhat similar systems.

In these experiments the electrodes remained constant in potential to 0.02 mv. for periods longer than the cells were studied.

The next junction studied was that contained in the cell

Ag–AgCl–0.10 *M* HCl / satd. KCl–HgCl–Hg

It was made in a manner similar to the one just described. In this case it was necessary, however, to adjust the solutions to the same hydrostatic pressure. Leaks in these cells were found especially troublesome when the junctions were flowed and all places had to be absolutely air-tight. The importance of keeping the potassium chloride solution saturated, as pointed out by Scatchard,[4] was observed here and to ensure this, crystals of potassium chloride were kept in the lower tube leading to the stopcock. Three

[8] Scatchard and Buehrer, THIS JOURNAL, 53, 574 (1931).

cells were measured first with static and then with flowing junctions. The average potentials of the three static junctions were 44.76, 44.76 and 44.75 mv., respectively, with a mean average deviation over forty-eight hours of ±0.02 mv. The results obtained with the flowing junction are represented graphically in Fig. 2.

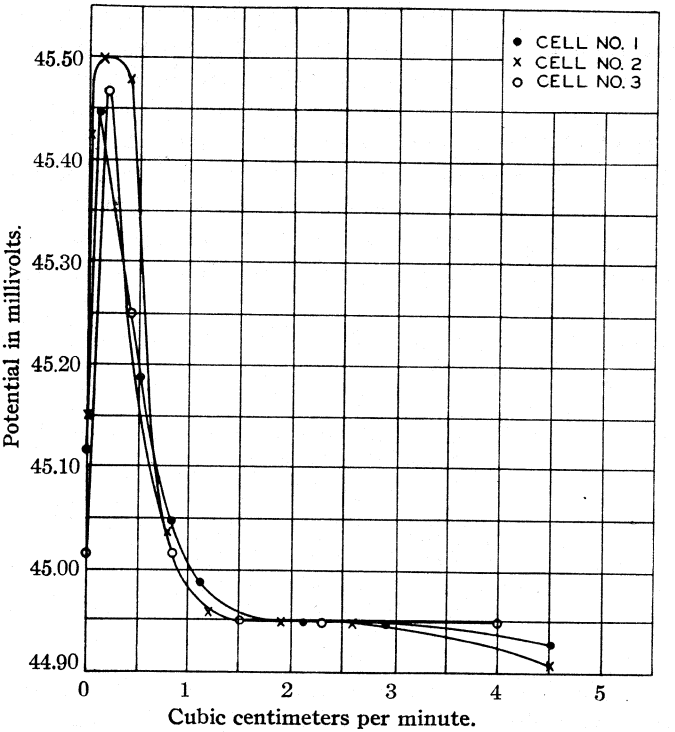


Fig. 2.—Curves showing the variations with the rate of flow of the potentials of the cells Ag–AgCl–0.10 *M* HCl/satd. KCl–HgCl–Hg.

It is evident, immediately, that the potentials vary greatly with the rate of flow and rise to a maximum at low rates. This maximum could be reproduced to 0.05 mv. and could be approached equally well from either direction. The potentials always decreased from the maximum when the flow was stopped, to values which might differ in separate experiments by 0.1 mv. and which were, on an average, about 0.1 mv. higher than the constant value at moderate rates. With rates of flow from 1.5 to 3.5 cc./min. the potentials were constant and reproducible in the different cells to 0.01 mv. For rates of flow greater than 3.5 cc./min. there was a slight decrease in potential. The constant potential obtained at medium rates of flow was about 0.2 mv. higher than the equally constant and reproducible value for the static junction obtained with identically the

same system before the flow was started. The shape of the curves was the same whether the rate of flow was varied from low to high or from high to low rates of flow.

Stirring the solutions in the outlet tube had no effect upon the potential until a point within 3 cm. of the stopcock itself was reached. From this point on the effect became greater until a maximum drop of 1.5 mv. was observed, when the solutions in the stopcock itself were completely mixed. This shows that the effective part of the junction is about the first 3 cm. of the horizontal tube.

The third junction studied was that in the cell

Ag–AgCl–0.01 *M* HCl / satd. KCl–HgCl–Hg

which is identical with the previous cell except for the concentration of the acid solution. Three cells of this type were run with static and flowing junctions. The averages of the three cells with static junctions were 99.04, 99.14 and 99.16 mv., respectively, with a mean average deviation of ±0.03 mv. for forty-eight hours. The potentials of the cells with flowing junctions are represented graphically in Fig. 3.

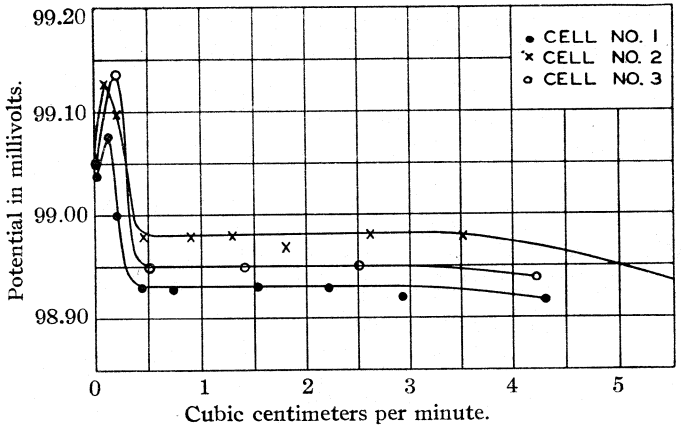


Fig. 3.—Curves showing the variations with the rate of flow of the potentials of the cells Ag–AgCl–0.01 *M* HCl/satd. KCl–HgCl–Hg.

In many respects the behavior of this junction is similar to the previous one, but in some respects it is distinctly different. There is an increase in potential at low rates and a slight decrease at high rates of flow. The values at medium rates are just as constant but less reproducible than those obtained with 0.10 *M* acid. There is also a decrease from the maximum when the flow is stopped, to a value about 0.1 mv. higher than that at medium rates of flow. When stirred, however, the junction with 0.01 *M* solution increased in potential 0.3 mv., while the 0.1 *M* decreased 1.5 mv.; also, with the 0.01 *M* solution the value at medium rates of flow

was 0.15 mv. lower than the average potential of the static junctions, while with the 0.10 *M* solution it was 0.2 mv. higher. These results indicate that saturated potassium chloride does not eliminate the boundary potential against hydrochloric acid solutions, that the remaining potential is different for different concentrations, and that it cannot be assumed that boundaries of different concentrations will respond in the same manner to disturbing influences.

## Summary

1. An apparatus has been developed for the direct comparison of static, flowing, "stopped flowing," and stirred junctions.

2. For concentration cells of 0.10 *M* and 0.01 *M* hydrochloric acid the potential is practically the same for all these types of junction.

3. For the junctions 0.10 *M* HCl / satd. KCl and 0.01 *M* HCl / satd. KCl the potential in each case depends upon the type of junction and the rate of flow, but these two junctions respond in opposite ways to certain treatments.

4. The effective part of this type of flowing junction is that contained in the first three cm. of the horizontal outlet tube.

5. For the systems involving saturated potassium chloride, the potentials with static junction are less empirical than those with flowing, because the variations of the potentials of the former with time are less than the variations of the latter with rate of flow.

ANN ARBOR, MICHIGAN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SYRACUSE UNIVERSITY]

# THE FREE ENERGY OF FORMATION OF ETHYL ACETATE. EQUILIBRIUM IN THE GASEOUS STATE[1]

BY HARRY ESSEX AND JOSEPH D. CLARK

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## Introduction

In this investigation the standard free energy change of the reaction

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

has been calculated at several temperatures from values of the equilibrium constant of the reaction in the gaseous state, which, together with data already available in the literature, leads to an evaluation of the standard free energy of formation of ethyl acetate.

Sabatier and Mailhe[2], working with metal oxides, reported that titanium oxide catalyzed only the esterification reaction in a gaseous mixture

[1] Submitted to the Faculty of Syracuse University by Joseph D. Clark in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, January, 1931.

[2] Sabatier and Mailhe, *Compt. rend.*, **152**, 669, 1044 (1911); **150**, 823 (1910); *Ann. chim. phys.*, **20**, 289, 351 (1910).

of an alcohol and an organic acid even at temperatures as high as 300°. With this catalyst, the authors claim to have reached equilibrium for the reaction in the gaseous state proceeding in either direction.[3] Sabatier reports a 70% esterification at 300°, which corresponds to a value of 5.4 for

$$K_p = \frac{P_{(\text{ester})} \times P_{(\text{H}_2\text{O})}}{P_{(\text{acid})} \times P_{(\text{alcohol})}}$$

at this same temperature.

Mailhe, and Mailhe and DeGodon[4] obtained data showing that zirconium oxide was exclusively an esterification catalyst. This conclusion was supported by the researches of Mailhe.[5] In this same paper it was claimed that equilibrium was reached starting from either side and using thoria as a catalyst. Mailhe did not attempt to purify completely his reagents and made no claim to a high degree of accuracy. For purposes of comparison, values of $K_p$ have been calculated from the concentrations at equilibrium in the separate experiments of Mailhe at the same temperature and found to differ from each other by several hundred per cent. Edgar and Schuyler[6] determined the composition of the vapors above an equilibrium liquid mixture. They found a value of $K_p$ for the gaseous equilibrium varying from 344 at 52.2° to approximately 500 at 77.6°. No high degree of accuracy was claimed by these authors. Swietoslawski and Poznanski,[7] using the same method but with some changes in technique, found $K_p$ to have a value of 59.0 and to be independent of temperature.

The results of Milligan, Chappell and Reid,[8] who first used silica gel as a catalyst, show a marked decrease in $K_p$ with increasing temperature. While the work to be described in the present paper was in progress, Tidwell and Reid[9] presented data for this same reaction showing a decrease in $K_p$ with increase in temperature, confirming the conclusions of Milligan, Chappell and Reid. Using the same catalyst they obtained the results given in Table I.

TABLE I

ESTERIFICATION DATA

| | Per cent. of esterification | | | |
|---|---|---|---|---|
| | 150° | 200° | 250° | 300° |
| From acid side | 84.2 | 82.6 | 77.7 | 74.2 |
| From ester side | 85.2 | 84.0 | 78.5 | 75.5 |

[3] Sabatier and Mailhe, *Compt. rend.*, **152**, 358, 949–97 (1911); Sabatier, "La Catalyse en Chimie Organique," C. Beranger, 1922, p. 297, 2d ed.

[4] Mailhe, *Caoutchouc et gutta-percha*, **18**, 10,679 (1921); *Chem. Abstracts*, **15**, 1023; Mailhe and DeGodon, *Bull. soc. chim.*, **29**, 101 (1921).

[5] Mailhe, *J. usines gaz.*, **48**, 17–21 (1924); *Chem. Abstracts*, **18**, 1419 (1924).

[6] Edgar and Schuyler, THIS JOURNAL, **46**, 64 (1924).

[7] Swietoslawski and Poznanski, *Roczniki Chem.*, **8**, 527 (1929); *Chem. Abstracts*, **23**, 2093 (1929).

[8] Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924).

[9] Tidwell and Reid, THIS JOURNAL, **53**, 4353 (1931).

The figures obtained in approaching the equilibrium from opposite directions differ appreciably.

Assuming that the reactants were in the ratio of one mole of acid to one mole of alcohol, $K_p$ calculated from the average of the limits of esterification from both directions has the values indicated in Table II.

TABLE II

VALUES OF $K_p$

| Temp., °C. | Ester at equilibrium, % | $K_p$ |
|---|---|---|
| 150 | 84.7 | 30.64 |
| 200 | 83.3 | 24.88 |
| 250 | 78.1 | 12.75 |
| 300 | 74.8 | 8.81 |

According to a recent article by Frolich, Carpenter and Knox,[10] the equilibrium position is at 87.5% of a mole of ethyl acetate at 280°, corresponding to a value of 49 for $K_p$, and 88.8% at 300°.

## Experimental Part

### A. Preparation of Pure Reagents

**Alcohol.**—Commercial ethyl alcohol was purified by the method of Brunel.[11] Only that fraction distilling over within 0.1° was accepted for use in this investigation. This purified alcohol had a specific gravity at 25° compared to water at 4° of 0.789305, which corresponds to 99.916% of alcohol. The alcohol was transferred to the pycnometer in an atmosphere of dry nitrogen. The 95.74% alcohol used in making up the reaction mixtures was prepared by dilution with water.

**Acetic Acid.**—The acid used was a product from the General Chemical Company labeled 99.55% acid. The only impurity indicated was water. This was purified by a method outlined in Allen's "Commercial Organic Analysis" (Vol. I, p. 643) under "Acetic Acid." The portion distilling within 1.5° was used. The specific gravity corresponded to 99.96% acid.

**Ethyl Acetate.**—This was a "C. P." product from the Eastman Kodak Company. It was fractionally distilled through a fractionating column, approximately 80% distilling over within a range of 1.0°; specific gravity, $d_4^{20}$ 0.9003.

**Base.**—Barium hydroxide was used to follow the progress of the esterification reaction. It was standardized by weight titration against the 99.96% acetic acid.

**Water.**—Only twice distilled water was used.

**Catalyst.**—The silica gel was the commercial product from the Silica Gel Corporation of Baltimore, Md. It was used without further treatment.

### B. Apparatus and Procedure

A diagram of the apparatus is shown in Fig. 1. The air-bath was a box 61 × 61 × 122 cm. inside measurements, built from 13-cm. 80% magnesia slabs buffered on the inside by 3.8-cm. Kieselguhr slabs and cemented together by asbestos cement. Heat was supplied by a series of 10-cm. nichrome heaters of the type used in electric radiators, placed in the bottom of the box and as far removed from the reaction tube as the inner space would permit. The temperature was controlled by the volume changes

[10] Frolich, Carpenter and Knox, THIS JOURNAL, 52, 1565 (1930).

[11] Brunel, *ibid.*, 45, 1334 (1923); 43, 561 (1921).

of a nitrogen reservoir. Only an approximate automatic control was possible because of barometric changes. For at least one-half hour preceding and throughout any one run the temperature was kept constant to within $\pm 0.1°$, manually. The air medium of the bath was kept in circulation by means of a 15-cm. motor-driven fan. Thermometers placed in various parts of the bath in the region of the reaction tube showed a maximum difference of 0.1°.

Equilibrium was determined by a dynamic method. The reactants entered the reaction chamber from bulb "A." To ensure a constant flow through the glass stopcock regulator a positive gas pressure of about one-third of an atmosphere was maintained above the reaction mixture. Nitrogen, which has no effect on the reactants, was used for this purpose. The reaction mixture was vaporized in a bead-filled preheater, which had the neck and side arm thoroughly insulated to prevent condensation.

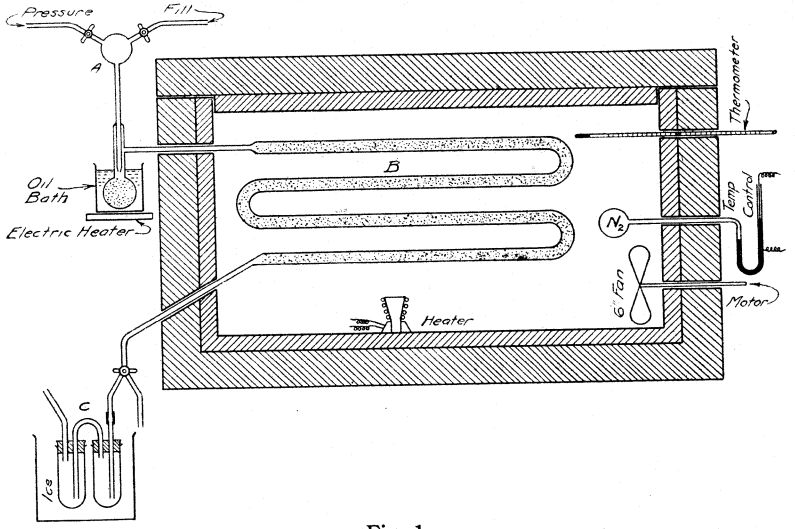


Fig. 1.

The reaction tube "B" was constructed from about 9.5 meters of 18-mm. Pyrex tubing sealed into one continuous coil. The original 1100 g. of silica gel required to fill the tube was used throughout the investigation. The products were collected through a delivery tube in two tared 3.8 × 15 cm. test-tubes in series. The collection tubes were cooled by ice. The collected product, test-tubes and fittings were weighed and the weight of the product determined. The contents were then carefully washed into a beaker and weight-titrated against the standard barium hydroxide solution. The concentration of the other constituents was calculated from the acid concentration of the product and the composition of the reaction mixture. The formation of gaseous products or a positive test for aldehydes was accepted as sufficient evidence of decomposition reactions.

At the beginning of any run or with each change of ratio of the reactants, the gaseous mixture was passed through the reaction tube until the concentration of the acid in the product became constant. In some cases it required two or three days and never less than 400 cc. of the reactants were used for this purpose.

## C. Preliminary Experiments

Before attempting a study of the equilibrium, the stability of the reactants, except water, was tested relative to heat. Each substance, in the gaseous state, was passed

through the reaction chamber, void of catalyst, at a temperature of about 350°. In no case could any decomposition be detected. The maximum temperature was then determined at which a mixture of the reactants could be passed over the catalyst without decomposition. The products were collected in an ice cooled receiver. At about 225° very small amounts of uncondensed gases were produced. These gases consisted of unsaturated compounds, as shown by complete absorption when tested with bromine water or fuming sulfuric acid. At higher temperatures the presence of aldehydes was indicated by the ammoniacal silver oxide and sodium bisulfite tests. Whenever decomposition occurred it was noted that carbon was deposited upon the catalyst. This deposited carbon seemed further to promote decomposition. It was removed from the catalyst by treatment with oxygen at a temperature of about 300° after all the reaction gases had been expelled by air. The oxygen was then displaced and the catalyst thoroughly saturated with nitrogen. This cleaning method was satisfactory and apparently had no detrimental effect upon the catalytic action of the silica gel.

## D. The Equilibrium Measurements

The equilibrium was determined at three temperatures, 150, 165 and 200°. At each temperature, after an approximate determination of the equilibrium position by preliminary experiments, carefully controlled runs were made with (a) a reaction mixture richer in alcohol and acid than the equilibrium mixture, (b) a reaction mixture richer in ester and water than the equilibrium mixture and (c) a reaction mixture having exactly the equilibrium concentrations as calculated from the average composition of the products of the runs (a) and (b). Each reaction mixture was made up in proportions which would be reached at some stage in the reaction

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

TABLE III

RESULTS OF EXPERIMENTS

Reaction mixture ratios $CH_3COOH$, 0.16 mole; $C_2H_5OH$, 0.16 mole; $CH_3COOC_2H_5$, 0.84 mole; $H_2O$, 0.84 mole. 150°C. Weight per cent. of acid in the reaction mixture, 9.05.

| Duration of run, min. | Wt. of product collected, g. | Wt. of base required to neutralize product, g. | Wt. % of acid in product |
|---|---|---|---|
| 60 | 11.1526 | 45.9595 | 8.78 |
| 60 | 8.8483 | 36.1264 | 8.70 |
| 120 | 5.0493 | 20.7048 | 8.74 |
| 240 | 10.2164 | 41.4298 | 8.65 |
| 90 | 3.9230 | 15.9315 | 8.66 |
| 210 | 9.0407 | 36.8308 | 8.69 |
| 240 | 6.4205 | 26.0948 | 8.67 |
| 135 | 4.3924 | 18.1483 | 8.81 |
| 120 | 6.1928 | 25.6064 | 8.83 |
| 120 | 6.1619 | 25.3752 | 8.87 |
| 240 | 10.1200 | 41.6031 | 8.76 |
| 150 | 14.4505 | 59.4433 | 8.77 |
| | | Average, | 8.74 |

$$K_a \left( K_a = \frac{a_{(\text{ester})}\, a_{(H_2O)}}{a_{(\text{acid})}\, a_{(\text{alcohol})}} \right) \text{ for average} = 33.69$$

if the initial mixture contained alcohol and acid alone in the proportion 1 mole of alcohol to 1 mole of acid. Runs were made over a considerable range of rates of flow with each reaction mixture at each temperature. The results of the run at 150° from the acid rich side are presented in detail in Table III. The results of the runs at this temperature and at 165 and 200° both of which were determined with a precision equal to that at 150, are presented in summary in Table IV.

TABLE IV

SUMMARIES OF RESULTS

| Temp., °C. | Wt. per cent. of acid in reaction mixture | Av. wt. of acid in product | $K_a$ |
|---|---|---|---|
| 150 | 8.48 | 8.75 | 33.61 |
| | 8.77 | 8.76 | 33.55 |
| | 9.05 | 8.74 | 33.69 |
| 165 | 9.05 | 9.56 | 26.36 |
| | 9.62 | 9.55 | 26.39 |
| | 10.18 | 9.55 | 26.39 |
| 200 | 8.48 | 11.51 | 15.98 |
| | 11.31 | 11.47 | 16.10 |
| | 14.14 | 11.46 | 16.13 |

The probable error in the determination of the percentage of acid at each temperature was calculated by the method of least squares.

The results of all the equilibrium determinations have been summarized in Table V. The probable errors in the average percentage of esterification are tabulated in column 3 of Table V.

TABLE V

PROBABLE ERRORS

| Temp., °C. | Average percentage of acid in products | Probable error in data of column 2 | Average values of $K_a$ |
|---|---|---|---|
| 150 | 8.75 | 0.0107 | 33.62 |
| 165 | 9.55 | .0056 | 26.38 |
| 200 | 11.48 | .0067 | 16.07 |

## Calculations

### A. Molal Composition of the Equilibrium Mixtures

**1. The Number of Moles of Each Constituent.**—At the temperatures at which measurements were made, no products were detected other than those entering into the reaction

$$CH_3COOH(g) + C_2H_5OH(g) = CH_3COOC_2H_5(g) + H_2O(g)$$

The molal composition of the gaseous mixture leaving the reaction tube was calculated from the composition of the entering mixture and the acid in the product.

For example, in one experiment at 150° the mixture entering the reaction

tube contained 9.05% of acetic acid, corresponding to the following number of formula weights of each constituent per 100 g. of the mixture

| | | | |
|---|---|---|---|
| Acid | 0.15080 | Ester | 0.79165 |
| Alcohol | .15080 | Water | .79165 |

This mixture was passed over the heated catalyst. The final product, after constancy in the acid percentage had been reached, analyzed 8.74% of acetic acid. This shows a shift of the equilibrium in the direction of ester and water formation, and corresponds to a decrease of 0.0052355 formula weights of acid and of alcohol per 100 g. and a like increase in the number of formula weights of ester and water. Therefore, in this final product, there were 0.145565 formula weights of acid and alcohol, and 0.7969 formula weights of ester and water. For alcohol, ester and water, the formula weights are the number of moles and these are listed in Table IX, in the columns headed $n_3$, $n_4$ and $n_5$, respectively.

An examination of the volume–pressure data of Ramsay and Young[12] indicates that even at a temperature of 184.1° and 0.12 atmosphere, acetic acid exists partly as double molecules. At lower temperatures, even higher complexity is indicated.

The association constant of the reaction

$$2CH_3COOH(g) = (CH_3COOH)_2(g)$$

is given by the relation

$$K_x = \frac{P_{(CH_3COOH)_2}}{P^2_{(CH_3COOH)}} \qquad (1)$$

where $P_{(CH_3COOH)_2}$ is the partial pressure of the double molecules of acetic acid, and $P_{(CH_3COOH)}$ is the partial pressure of the single molecules, and may be calculated from the data of Ramsay and Young.[12]

The number of moles of $CH_3COOH$ ($n_1$) and $(CH_3COOH)_2$ ($n_2$) per 100 g. of our reaction product may be calculated from this $K_x$ and the number of moles of alcohol ($n_3$), ethyl acetate ($n_4$), water ($n_5$), and the number of formula weights of acetic acid ($w$). The partial pressures of $(CH_3COOH)_2$ and $CH_3COOH$ in our products are given, respectively, by the equations

$$P_{(CH_3COOH)_2} = \frac{n_2}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \qquad (2)$$

and

$$P_{(CH_3COOH)} = \frac{n_1}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \qquad (3)$$

1 being the total pressure in atmospheres of these experiments. That is, each partial pressure is the product of the mole fraction and the total pressure. Substituting these values into equation 1

$$K_x = \frac{n_2(n_1 + n_2 + n_3 + n_4 + n_5)}{n_1^2} \qquad (4)$$

[12] Ramsay and Young, *J. Chem. Soc.*, **49**, 790 (1886); "International Critical Tables," Vol. III, p. 437.

If $G$ is the weight of acetic acid in the equilibrium products, then $G = 60.03n_1 + 120.06n_2$ and

$$w = \frac{G}{60.03} = n_1 + 2n_2$$

or

$$n_2 = \frac{w - n_1}{2} \qquad (5)$$

Upon substituting the value of $n_2$ (equation 5) into equation 4

$$K_x = \frac{\frac{w - n_1}{2}\left(n_1 + \frac{w - n_1}{2} + n_3 + n_4 + n_5\right)}{n_1^2}$$

from which

$$n_1 = \pm\sqrt{\frac{2w}{4K_x + 1}\left(\frac{w}{2} + n_3 + n_4 + n_5\right) + \left(\frac{n_3 + n_4 + n_5}{4K_x + 1}\right)^2} - \frac{n_3 + n_4 + n_5}{4K_x + 1} \qquad (6)$$

In order that $n_1$ be positive, the sign preceding the square root must be positive. This expression (equation 6) may be used to find the number of single moles of acetic acid ($n_1$) in the equilibrium mixture from its percentage composition. The number of double moles of acetic acid ($n_2$) may be obtained by substituting the numerical value of $n_1$ into equation 5.

**2. Evaluation of $K_x$ at the Temperatures of the Experiments.**—The pressure–volume data for acetic acid of Table VI were taken from "International Critical Tables."[12] In Table VI, $P$ is expressed in atmospheres, $V$ in liters per gram, and $T$ in degrees absolute.

TABLE VI

| | | | |
|---|---|---|---|
| $T$ | 457.2 | 391.1 | 351.5 |
| $PV$ | 0.605 | 0.436 | 0.302 |

Let $M$ equal the average molecular weight. Then

$$M = \frac{RT}{PV} \qquad (7)$$

and for the data at $T = 457.2$, $M = 62.05$, the molecular weight of the acetic acid.

If $\alpha$ represents the degree of dissociation of gaseous acetic acid double molecules, and $M_0$ the molecular weight of the double molecules, then

$$\alpha = \frac{M_0 - M}{M} \qquad (8)$$

or, by substitution

$$\alpha = \frac{120.06 - 62.05}{62.05} = 0.9355$$

That is, at 457.2°K. and 0.12 atmosphere $(CH_3COOH)_2$ is 93.55% dissociated.

The equilibrium constant for the reaction

$$2CH_3COOH(g) = (CH_3COOH)_2(g)$$

is related to the degree of dissociation by the expression

$$K_x = \frac{1 - \alpha^2}{4\alpha^2 P} \tag{9}$$

from which

$$K_x = 0.303 \text{ at } T = 457.2°\text{K.}$$

In a similar manner $K_x$, at two additional temperatures, was calculated. The values of these are presented in Table VII.

TABLE VII

| | | | |
|---|---|---|---|
| $T$ | 457.2 | 391.1 | 351.5 |
| $PV$ | 0.605 | 0.436 | 0.302 |
| $M$ | 62.05 | 73.64 | 95.57 |
| $\alpha$ | 0.9347 | 0.6301 | 0.2562 |
| $K_x$ | .303 | 3.164 | 29.66 |

From these values, $K_x$ is given as a function of temperature by the relation (throughout this paper, ln = $\log_e$, while log = $\log_{10}$)

$$\log K_x = \frac{8082}{T} + 29.12 \log T - 95.653 \tag{10}$$

Substituting for $T$ the desired temperature and solving for $K_x$ the results of Table VIII were computed.

TABLE VIII

| | | | |
|---|---|---|---|
| $T$ | 423.1 | 438.1 | 473.1 |
| $K_x$ | 0.8512 | 0.5224 | 0.2104 |

The values of $K_x$ and $n_1$ calculated from equation 6, $n_2$ calculated from equation 5, and $n_3$, $n_4$ and $n_5$ are listed in Table IX.

TABLE IX

| $T$ | $K_x$ | $w$ | $n_1$ | $n_2$ | $n_3$ | $n_4$ | $n_5$ |
|---|---|---|---|---|---|---|---|
| 423.1 | 0.8512 | 0.145898 | 0.1300 | 0.0080 | 0.1459 | 0.7966 | 0.7966 |
| | | .145731 | .1303 | .0077 | .1457 | .7968 | .7968 |
| | | .145565 | .1302 | .0077 | .1456 | .7968 | .7968 |
| 438.1 | .5224 | .15906 | .1470 | .0060 | .1591 | .7834 | .7834 |
| | | .15922 | .1472 | .0060 | .1592 | .7833 | .7833 |
| | | .15906 | .1470 | .0060 | .1591 | .7834 | .7834 |
| 473.1 | .2104 | .19170 | .1814 | .0038 | .1917 | .7508 | .7508 |
| | | .19103 | .1833 | .0039 | .1901 | .7515 | .7515 |
| | | .19087 | .1834 | .0037 | .1909 | .7516 | .7516 |

**B. Activities of the Constituents of the Mixture at Equilibrium.**— For the esterification reaction under consideration the activity equilibrium constant $K_{(a)}$ is

$$K_{(a)} = \frac{a_4 \times a_5}{a_1 \times a_3} \tag{11}$$

in which $a_1$, $a_3$, etc., are the activities of the acid, alcohol, ester and water, respectively, in the equilibrium mixture.

At the low total pressure of these experiments, namely, one atmosphere, and the low partial pressure of the several constituents of the resulting mixture at equilibrium, it is justifiable to substitute for the activities of the alcohol, ester and water in the gaseous mixture their mole fractions, and equation 11 becomes

$$K_{(a)} = \frac{N_4 \times N_5}{a_1 \times N_3} \tag{12}$$

The results of Gibson and Sosnick[13] support this assumption. For mixtures of ethylene and argon, the experimental data used by these writers indicate practical identity of fugacity and mole fraction at one atmosphere of pressure. The assumption is further justified by the experimental results obtained by Lurie and Gillespie[14] for mixtures of ammonia and nitrogen.

These mole fractions are

$$N_3 = \frac{n_3}{n_1 + n_2 + n_3 + n_4 + n_5}$$

$$N_4 = \frac{n_4}{n_1 + n_2 + n_3 + n_4 + n_5} \text{ etc.}$$

The activity or fugacity of the acetic acid in the equilibrium mixture may be calculated in the following manner.

For the reaction

$$2CH_3COOH(g) = (CH_3COOH)_2(g)$$

from equation 9

$$\alpha = \left(\frac{1}{4K_xP + 1}\right)^{1/2} \tag{13}$$

in which $P$ is the total pressure of the acetic acid. For brevity during this derivation, $K_x$ will be designated simply as $K$.

For a formula weight of acetic acid vapor

$$PV = \frac{1 + \alpha}{2} RT$$

Combining this with equation 13

$$V = \frac{RT}{2P} + \frac{1}{2}\left(\frac{1}{4KP + 1}\right)^{1/2} \frac{RT}{P} \tag{14}$$

Substituting the value of $V$ from equation 14 into the relation

$$\int RT \, d \ln f = \int V \, dP$$

then

$$\int RT \, d \ln f = \int \frac{RT}{2P} \, dP + \frac{RT}{2} \int \left(\frac{1}{4KP + 1}\right)^{1/2} \frac{dP}{P} \tag{15}$$

which on integration between the very low pressure $P^*$ and $P$ gives

$$RT \ln f - RT \ln f^* = \frac{RT}{2} \ln P - \frac{RT}{2} \ln P^* + \frac{RT}{2} \ln \frac{[(4KP + 1)^{1/2} - 1]}{[(4KP + 1)^{1/2} + 1]} - \frac{RT}{2} \ln \frac{[(4KP^* + 1)^{1/2} - 1]}{[(4KP^* + 1)^{1/2} + 1]} \tag{16}$$

[13] Gibson and Sosnick, THIS JOURNAL, **49**, 2172 (1927).

[14] Lurie and Gillespie, *ibid.*, **49**, 1146 (1927).

At the very low pressure $P^*$, $4KP^*$ is always less than unity, and $(1 + 4KP^*)^{1/2}$ may be expanded by the binomial theorem, becoming $(1 + 2KP^*)$ and

$$\ln f = \frac{1}{2} \ln \frac{P}{K} \frac{[(4KP + 1)^{1/2} - 1]}{[(4KP + 1)^{1/2} + 1]} \tag{17}$$

In equation 17 (Note.—Although equation 17 was derived for the association of gaseous acetic acid, it is a perfectly general equation, applicable to any simple association of the type, double molecules in equilibrium with single molecules, and may be used to calculate the fugacity of such a gas at any pressure from the association constant), $K$ is the quantity previously indicated by $K_x$. The fugacity of the acetic acid gas in the equilibrium mixtures of these experiments may be calculated from equation 17 by substituting for $K$ the association constant of acetic acid at the temperature of the experiment and for $P$ the partial pressure of the acetic acid gas, which is equal to the sum of the partial pressures of the single and double molecules, and given by the expression

$$P_{(acid)} = \frac{n_1 + n_2}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \tag{18}$$

The values of $P_{(acid)}$ and $K_x$ of Table X, when substituted into equation 17, give the values for the fugacity of acetic acid, $f_{(acid)}$, listed in this same table.

TABLE X

| $T$ | $K_x$ | $P_{(acid)}$ | $f_{(acid)}$ | $N_2$ | $N_4$ | $N_5$ | $K_a$ | Average $K_a$ | $\Delta F^\circ$ from $K_a$ |
|---|---|---|---|---|---|---|---|---|---|
| 423.1 | 0.8512 | 0.0735 | 0.0691 | 0.07765 | 0.4242 | 0.4242 | 33.55 | | |
| | | .0735 | .0691 | .07760 | .4245 | .4245 | 33.61 | 33.62 | −2957.4 |
| | | .0734 | .0690 | .07755 | .4245 | .4245 | 33.69 | | |
| 438.1 | .5224 | .0814 | .0778 | .08462 | .4168 | .4168 | 26.39 | | |
| | | .0815 | .0779 | .08468 | .4169 | .4169 | 26.36 | 26.38 | −2851.3 |
| | | .0814 | .0778 | .08462 | .4168 | .4168 | 26.39 | | |
| 473.1 | .2104 | .0999 | .0979 | .1019 | .3992 | .3992 | 15.98 | | |
| | | .0996 | .0976 | .1016 | .3996 | .3996 | 16.10 | 16.07 | −2612.4 |
| | | .0995 | .0975 | .1015 | .3995 | .3995 | 16.13 | | |

## C. Equilibrium Constant and Standard Free Energy Change of the Gaseous Reaction

**Heat of Gaseous Reaction.**—At any temperature, the standard free energy change, $\Delta F^\circ$, of a reaction is related to the activity equilibrium constant by the equation

$$\Delta F^\circ = -RT \ln K_a \tag{19}$$

By substituting the numerical values of $K_a$ and the corresponding temperatures, the values of $\Delta F^\circ$ listed in Table X were calculated.

The maximum variation in the $\Delta F^\circ$ values for any one temperature is 13 calories.

Expressing $\Delta F^\circ$ as a function of temperature by means of

$$\Delta F^\circ = \Delta H_0 - \Delta\Gamma_0 T \ln T + IT \qquad (20)$$

and solving three simultaneous equations involving the values of $\Delta F^\circ$ from the experimentally determined equilibrium constants, the following equation was obtained

$$\Delta F^\circ = -8385 - 5.06\ T \ln T + 46.70T \qquad (21)$$

From equation 21, $\Delta F^\circ_{(298.1)}$ equals $-3975.1$ calories, or $K_a$ equals 817.3.

The heat of the reaction, $\Delta H$, may be calculated by plotting $R \ln K_a$ against $1/T$. This has been done in a curve of Fig. 2. The individual

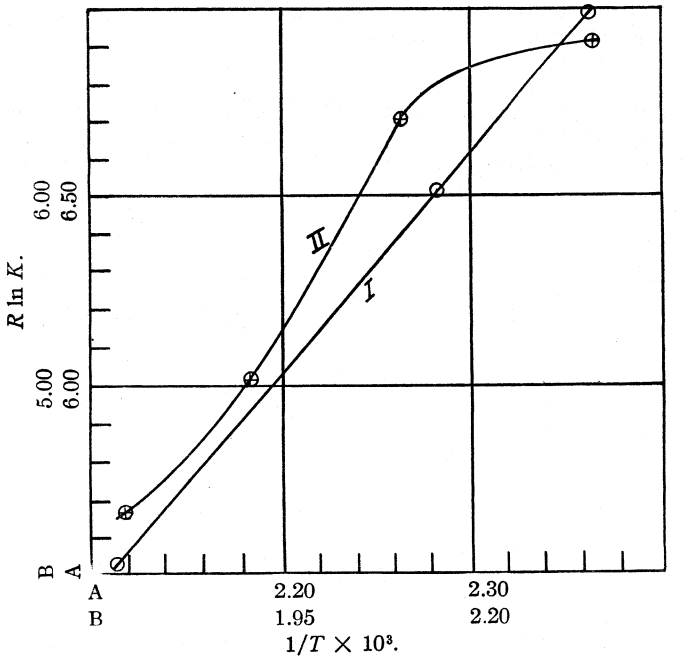


Fig. 2.—Curve I, A axes. Curve II, B axes.

points fall upon a curve (Curve I) which is very nearly a straight line, showing that the heat of the reaction is practically independent of the temperature. The negative values of the slope of the curve, $\Delta H$, at different temperatures are listed.

| | | |
|---|---|---|
| Temperature, °C. | 157.5 | 182.5 |
| $\Delta H$ in calories | −5935.3 | −5825.0 |

A similar curve constructed from the results of Tidwell and Reid (Curve II), exhibits double flexure. On substituting the previously determined values $\Delta H_0$ and $\Delta\Gamma_0$ into the integrated form of Kirchhoff's equation

$$\Delta H_{(298.1°)} = -6716.4 \text{ calories}$$

## D. Standard Free Energy Change on Vaporization of the Liquid Constituents

**Heats of Vaporization.**—The vapor pressure data of Table XI are taken from the Critical Tables.[15]

TABLE XI

| $T$ | Vapor pressure for alcohol, mm. | Vapor pressure for ethyl acetate, mm. |
|---|---|---|
| 293.1 | 43.9 | 72.8 |
| 303.1 | 78.8 | 118.7 |
| 313.1 | 135.3 | 186.3 |

From each vapor pressure the standard free energy change on vaporization was calculated from the relation

$$\Delta F^\circ = -RT \ln P$$

From the three values of $\Delta F^\circ$ obtained in this manner for the vaporization of each liquid, the constants $\Delta H_0$, $\Delta \Gamma_0$, and $I$ were found by solving the three equations of the form

$$\Delta F^\circ = \Delta H_0 - \Delta \Gamma_0 T \ln T + IT \qquad (22)$$

for the unknowns. The standard free energy change on vaporization at 298.1°K. was then calculated from equation 22 and the heat of vaporization at the same temperature from the constants $\Delta H_0$ and $\Delta \Gamma_0$ and the equation

$$\Delta H = \Delta H_0 + \Delta \Gamma_0 T$$

For alcohol, the values of the constants are: $\Delta H_0 = 14502.8$; $\Delta \Gamma_0 = -13.95$; and $I = -123.067$; and for the reaction

$$C_2H_5OH(l) = C_2H_5OH(g)$$

$\Delta F^\circ_{(298.1)} = 1513.5$ cal. and $\Delta H_{(298.1)} = 10{,}344.3$ cal.

For ethyl acetate, the values of the constants are: $\Delta H_0 = 13692.2$; $\Delta \Gamma_0 = -16.833$; and $I = -137.68$. And for the reaction

$$CH_3COOC_2H_5(l) = CH_3COOC_2H_5(g)$$

$\Delta F^\circ_{(298.1)} = 1244.2$ cal. and $\Delta H_{(298.1)} = 8674.3$ cal.

For the reaction

$$H_2O(l) = H_2O(g)$$

the standard free energy change and heat of vaporization were taken directly from the Critical Tables, and are: $\Delta F^\circ_{(298.1)} = 2053$ cal.; $H_{(298.1)} = 10{,}450$ cal.

Saturated acetic acid vapor is highly associated at 298.1°K. Its vapor pressure therefore cannot be substituted for its activity. Neither can its fugacity or activity be calculated by equations 8, 9 and 17, nor by the extrapolation equation 10, because these methods are justified if the acetic acid vapor contains only double and single molecules. The vapor density of saturated acetic acid vapor at 298.1°K. is sufficiently high that molecules

[15] "International Critical Tables," Vol. III, pp. 217, 219.

of higher complexity than that of double molecules may be present in considerable concentration.

The fugacity of the saturated acetic acid vapor at 298.1°K. was finally determined by an indirect method. The fugacity was first calculated at the three temperatures, 351.5, 378.2 and 406.0°K., in the following manner: using $P$–$V$–$T$ data of Ramsay and Young,[12] the fugacity of acetic acid vapor at each of these temperatures was calculated at the respective pressures of 0.1200 atmosphere, 0.1238 atmosphere, and 0.1338 atmosphere by equation 17 and the fugacity of saturation from the relation

$$\log f_{p_2} = \frac{A}{2.303\,RT} + \log f_{p_1}$$

in which $f_{p_2}$ is the fugacity at the saturation pressure at the temperature $T$, $f_{p_1}$ the fugacity at the lower pressure at which it was determined by equation 17. $A$ is the area under the $P$–$V$ curve from $P_1$ to $P_2$.

This method should give the correct fugacity of the saturated vapor even though molecules of high complexity are present in the saturated vapor, provided that single and double molecules only are present at the lower pressure $P_1$. In each case the density of the gas at $P_1$ was sufficiently low to indicate that this was probably true. The lowest pressures given in the data of Ramsay and Young were not picked for $P_1$ because of the apparently large experimental errors involved in the density measurements at these very low pressures. The data and results of these calculations are presented in Table XII.

TABLE XII

| $T$, °K. | $P_1$, atm. | $P_2$, atm. | $K_x$ | $A$, liter-atm. | $f_{p_1}$ | $f_{p_2}$ |
|---|---|---|---|---|---|---|
| 351.5 | 0.1200 | 0.2500 | 29.66 | 12.54 | 0.048945 | 0.0756 |
| 378.2 | .1238 | .6775 | 6.23 | 36.55 | .081956 | .2659 |
| 406.0 | .1338 | 1.540 | 1.567 | 56.97 | .11359 | .6273 |

From the values of the fugacity of the saturated vapors at the three temperatures, the standard free energy change on vaporization was calculated from

$$\Delta F^\circ = -RT \ln f$$

The values obtained are: $\Delta F^\circ_{(406.0)} = 376.5$; $\Delta F^\circ_{(378.2)} = 996.2$ $\Delta F^\circ_{(351.5)} = 1804.9$.

$\Delta F^\circ_{(406.0)} = 376.5$; $\Delta F^\circ_{(378.2)} = 996.2$ $\Delta F^\circ_{(351.5)} = 1804.9$

which, upon substitution in the relation

$$\Delta F^\circ = \Delta H_0 - \Delta\Gamma_0 T \ln T + IT$$

gives the values of the constants indicated by

$$\Delta F^\circ = 55{,}071 + 116.671T \ln T - 835.6$$

from which, for the reaction

$$CH_3COOH(l) = CH_3COOH(g)$$

$\Delta F^\circ_{(298.1)} = 4168.4$ cal. and $\Delta H^\circ_{(298.1)} = 20291.4$ cal.

## E. Standard Free Energy Change of the Liquid Reaction. The Free Energy of Formation of Ethyl Acetate

**(1) Standard Free Energy Change of the Liquid Reaction.**—By combining algebraically the vaporization equation of each pure constituent and the esterification reaction in the gaseous state, the standard free energy change for the esterification reaction in the liquid state may be calculated.

$CH_3COOH(g) + C_2H_5OH(g) = CH_3COOC_2H_5(g) + H_2O(g)$; $\Delta F^\circ_{(298.1)} = -3975.1$ cal.
$C_2H_5OH(l) = C_2H_5OH(g)$; $\Delta F^\circ_{(298.1)} = 1513.5$ cal.
$CH_3COOH(l) = CH_3COOH(g)$; $\Delta F^\circ_{(298.1)} = 4168.4$ cal.
$CH_3COOC_2H_5(g) = CH_3COOC_2H_5(l)$; $\Delta F^\circ_{(298.1)} = -1244.2$ cal.
$H_2O(g) = H_2O(l)$; $\Delta F^\circ_{(298.1)} = -2053$ cal.

---

$CH_3COOH(l) + C_2H_5OH(l) = CH_3COOC_2H_5(l) + H_2O(l)$; $\Delta F^\circ_{(298.1)} = -1590.4$ cal.
or $K_{a(298.1)}(1) = 14.63$

$K_a$, the true activity ratio, may be quite different from the concentration ratio, $K_c$. That they are not identical for this reaction is shown by the experimental results of Poznanski[16] and Schwab.[17] Poznanski, by varying the concentration of his reactants, found that for this reaction $K_c$ varied from 2.45 to 4.73. Schwab found $K_c$ to vary between 1.0 and 6.8.

**(2) The Free Energy of Formation of Ethyl Acetate.**—From heat capacity measurements at low temperatures, Parks, Kelley and Huffman[18] have computed, with the aid of the third law of thermodynamics, the standard free energy of formation of the following substances at 298.1°K. to be

Ethyl alcohol; $\Delta F^\circ = -43{,}200$ cal.
Acetic acid; $\Delta F^\circ = -95{,}400$ cal.

Allowing for the new value of the entropy of hydrogen, 31.23, as computed by Giauque,[19] these standard free energies of formation become:

Alcohol; $\Delta F^\circ = -41{,}900$
Acid; $\Delta F^\circ = -94{,}680$

The standard free energy of formation of water at 298.1°K. has been calculated by Lewis and Randall[20] and found to be

Water (l); $\Delta F^\circ = -56{,}560$ cal.

Using these values the standard free energy of formation of the ester was calculated to be −81,610.4 calories at 298.1°K.

## F. Heat of the Liquid Reaction

The heat of the reaction in the liquid state was obtained at 25° from the heats of vaporization of the various constituents as previously cal-

[16] Poznanski, *Chem. Abstracts*, **23**, 1559 (1922).
[17] Schwab, *Rec. trav. chim.*, **2**, 46 (1883).
[18] Parks, Kelley and Huffman, THIS JOURNAL, **51**, 1969 (1929).
[19] Giauque, *ibid.*, **52**, 4816 (1930).
[20] Lewis and Randall, "Thermodynamics," p. 485.

culated, and the $\Delta H$ for the reaction taking place in the gaseous state. Combining these algebraically

$$CH_3COOH(g) + C_2H_5OH(g) \overset{298.1^\circ}{=} CH_3COOC_2H_5(g) + H_2O(g); \quad \Delta H = -6716.4 \text{ cal.}$$

$$CH_3COOH(l) \overset{298.1^\circ}{=} CH_3COOH(g); \quad \Delta H = 20{,}291.4 \text{ cal.}$$

$$C_2H_5OH(l) \overset{298.1^\circ}{=} C_2H_5OH(g); \quad \Delta H = 10{,}344.3 \text{ cal.}$$

$$CH_3COOC_2H_5(g) \overset{298.1^\circ}{=} CH_3COOC_2H_5(l); \quad \Delta H = -8674.3 \text{ cal.}$$

$$H_2O(g) \overset{298.1^\circ}{=} H_2O(l); \quad \Delta H = -10{,}450 \text{ cal.}$$

---

$$CH_3COOH(l) + C_2H_5OH(l) \overset{298.1^\circ}{=} CH_3COOC_2H_5(l) + H_2O(l); \quad \Delta H = 4795.0 \text{ cal.}$$

Kharasch[21] made a general and critical review of the data to be found in the literature for heats of combustion. By using the data of his choice, the heat of the esterification reaction in the liquid state was calculated, as follows

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O; \quad \Delta H = -328{,}500 \text{ cal.}$$
$$CH_3COOH + 2O_2 = 2CO_2 + 2H_2O; \quad \Delta H = -208{,}250 \text{ cal.}$$
$$4CO_2 + 4H_2O = CH_3COOC_2H_5 + 5O_2; \quad \Delta H = 538{,}430 \text{ cal.}$$

---

$$C_2H_5OH(l) + CH_3COOH(l) \overset{298.1^\circ\text{K.}}{=} CH_3COOC_2H_5(l) + H_2O(l); \quad \Delta H_{(298.1^\circ\text{K.})} = 1630 \text{ cal.}$$

Kharasch estimated that the figures to be found in the literature for the heats of combustion may be in error by from 1.0 to 1.5%. It is to be noted that the value of the heat of the esterification reaction calculated from the heats of combustion of the several constituents of the reaction agrees with the heat of the reaction calculated from the equilibrium constants determined in this work, within the 1.0% error involved in the heat of combustion data.

### G. The Entropy of Ethyl Acetate

Because of the one per cent. error that may exist in the determined value of the heat of combustion of ethyl acetate, the entropy of ethyl acetate calculated by means of the equation

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

can be considered as no more than an approximation. Accepting 112,500 calories as the heat of formation of ethyl acetate

$$\Delta S_{(298.1^\circ)} = -96.85 \text{ calories}$$

and

$$S_{(298.1^\circ)} = 81.27$$

## Summary

1. Equilibrium has been reached in the gaseous phase for the system: acetic acid, ethyl alcohol, ethyl acetate and water, approaching it by a

[21] Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929).

dynamic method from both sides at the three temperatures, 423°K., 438°K. and 473°K.

2. The activity ratio $K_a$ has been calculated for the gaseous state equilibrium to be

| Absolute temp., °K. | 298.1 | 298.1 | 423.1 | 438.1 | 473.1 |
|---|---|---|---|---|---|
| State | Liquid | Gas | Gas | Gas | Gas |
| $K_a$ | 14.63 | 817.3 | 33.62 | 26.38 | 16.07 |

3. The standard free energy change for the esterification reaction calculated from the determined activity ratios is

| Absolute temp., °K. | 298.1 | 298.1 | 423.1 | 438.1 | 473.1 |
|---|---|---|---|---|---|
| State | Liquid | Gas | Gas | Gas | Gas |
| $\Delta F°$ in cal. | −1590.4 | −3975.1 | −2957.4 | −2851.3 | −2612.4 |

The standard free energy of formation of ethyl acetate in the liquid state at 298.1°K. is found to be −81,610.4 calories.

4. From the curve for the change of $K_a$ with temperature, the heat of the esterification reaction has been calculated for the gaseous state at two high temperatures. For the temperature of 298.1°K. it was calculated from Kirchhoff's equation for the gaseous state and from the vapor pressures and heat of the gaseous reaction for the liquid state. The results are

| Absolute temp., °K. | 298.1 | 298.1 | 430.5 | 455.5 |
|---|---|---|---|---|
| State | Liquid | Gas | Gas | Gas |
| Heat of the reaction, cal. | 4795.0 | −6716.4 | −5935.3 | −5825.0 |

5. The equation

$$\ln f = \frac{1}{2} \ln \frac{P}{K} \frac{[(4KP + 1)^{1/2} - 1]}{[(4KP + 1)^{1/2} + 1]}$$

has been developed for the calculation of the fugacity of a gas which is partially associated as double molecules.

SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, GRADUATE SCHOOL OF TROPICAL AGRICULTURE AND CITRUS EXPERIMENT STATION]

# THE UTILIZATION OF THE BASE-EXCHANGE REACTION FOR THE DETERMINATION OF ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTES

BY ALBERT P. VANSELOW

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In the course of an investigation of the cation-exchange reaction of the various types of alumino-silicates the author was impressed with the possibility of utilizing certain of the minerals known as bentonites for the determination of the relative activity coefficients in mixed electrolytes.

Bentonites[1] are a class of clay minerals of the general composition $(MO)_x \cdot Al_2O_3 \cdot (SiO_2)_y \cdot nH_2O$, in which $x$ has a value of 1 or somewhat less, and $y$ has a value of from 3 to 5. The cation M is for the main part magnesium, though it can consist in part of calcium, potassium and sodium. Bentonites occur as very minute micaceous crystals of colloidal dimensions, and they are practically insoluble in water and neutral salt solutions. The bentonites found most suitable for the investigation of activity coefficients are those which approximate the ideal montmorillonite type most closely, montmorillonite having the theoretical composition $MO \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$. About one-third of the cation M can be replaced by other cations simply by shaking or leaching the bentonite with a neutral salt solution, and for any one bentonite the fraction of M that can be thus replaced is a perfectly definite quantity.

A bentonite which has been treated with a solution of a particular cation to the point where it has taken up all of this cation that it is capable of is said to be saturated with this cation; and this cation in turn can be partially or wholly displaced by another. Under certain conditions this cation-exchange reaction of bentonites is entirely reversible. A bentonite saturated with the cation A when treated with a solution of some other cation B would react in the manner

$$AZ + B^+ = BZ + A^+$$

where the symbol Z is used to designate the insoluble complex anion of the bentonite. Given sufficient time for the system to attain equilibrium, the equilibrium conditions are represented by the equation

$$K = \frac{(A^+)}{(B^+)} \times \frac{(BZ)}{(AZ)} \qquad (A)$$

All quantities in parentheses are activities. The activities, (BZ) and (AZ), of the solid phases are easily evaluated. Data being published in a paper soon to appear elsewhere show that the partial substitution of one cation for another results in the formation of mixed crystals and not two in-

[1] C. S. Ross and E. V. Shannon, *J. Am. Ceram. Soc.*, **9**, 77 (1926).

dependent solid phases. Furthermore, the complex anion Z behaves as it if were monovalent. If AZ and BZ form mixed crystals, their activities are equal to their mole fractions and Equation A becomes

$$K = \frac{(A^+)}{(B^+)} \times \frac{\frac{BZ}{AZ + BZ}}{\frac{AZ}{AZ + BZ}} = \frac{(A^+)}{(B^+)} \times \frac{BZ}{AZ}$$

The quantity BZ/AZ is simply the ratio of the two cations in the solid phase. Introducing the activity coefficients of the ions in solution our equation can be written in the form

$$K = \frac{\gamma_{A^+}}{\gamma_{B^+}} \times \frac{A^+}{B^+} \text{ (in solution)} \times \frac{BZ}{AZ} \text{ (in solid phase)}$$

The constant $K$ can be evaluated in the following manner. Series of equilibria determinations are made at various concentrations, and the values of $K'$ calculated by means of the equation

$$K' = \frac{A}{B} \text{ (in solution)} \times \frac{BZ}{AZ} \text{ (in solid phase)}$$

are plotted against some function of the ionic strength and extrapolated to infinite dilution. The value of $K'$ at infinite dilution, designated by the symbol $K'_\infty$, is equal to the equilibrium constant $K$ of Equation A, for at infinite dilution

$$\gamma_{A^+} = 1 \quad \gamma_{B^+} = 1 \text{ and } \frac{\gamma_{A^+}}{\gamma_{B^+}} = 1$$

Since

$$K'_\infty = K = \frac{\gamma_{A^+}}{\gamma_{B^+}} \times K'$$

it follows that the ratio of the activity coefficients of the two cations at any concentration $c$ is equal to the ratio of $K'_\infty$ to $K'$ at that concentration, or

$$\left(\frac{\gamma_{A^+}}{\gamma_{B^+}}\right)_c = \frac{K'_\infty}{K'_c}$$

Thus, if we experimentally determine or arbitrarily assign values to the activity coefficients of one of the cations in the solution, we can calculate the activity coefficients of the other cation.

The number of cations in the system need not be restricted to two but can be as large as desired. In a system of cations, A, B, C, D, . . ., in equilibrium with a bentonite, the equilibrium relationships of any pair of cations can be used to calculate their relative activity coefficients. Thus each cation can in turn be compared with the standard cation, and the relative activity coefficients determined in mixed electrolytes of almost any degree of complexity.

The author's experimental application of this method for determining activity coefficients has been extremely limited by necessity. A few experiments have been conducted with the cadmium–barium exchange reaction.

The reaction was first investigated at a constant total concentration of 100 milliequivalents per liter and at a temperature of 25°. A series of eight experiments was performed, in which various amounts of barium-saturated bentonite were used and in which the relative amounts of barium and cadmium in the solutions were also varied, thereby covering the composition range fairly well. After two weeks of stirring in the thermostat they were permitted to settle, the clear supernatant solutions were siphoned off and analyzed for both cadmium and barium. These analytical results, the amounts of barium-saturated bentonite used, and the compositions of the initial solutions are given in Table I, along with the calculated data.

TABLE I

EXPERIMENTAL DATA FOR THE BARIUM–CADMIUM EXCHANGE REACTION AT CONSTANT IONIC STRENGTH

All concentrations expressed as milliequivalents per liter

| No. | Initial concns. | | | Final concns. By analysis | | Calculated | | $K'$ |
|---|---|---|---|---|---|---|---|---|
| | $Cd^{++}$ | $Ba^{++}$ | $BaZ_2$ | $Cd^{++}$ | $Ba^{++}$ | $CdZ_2$ | $BaZ_2$ | |
| 1 | 100 | 0 | 20 | 89.0 | 12.4 | 11.0 | 7.6 | 0.202 |
| 2 | 100 | 0 | 40 | 81.7 | 19.3 | 18.3 | 20.7 | .209 |
| 3 | 100 | 0 | 60 | 76.8 | 24.4 | 23.2 | 35.6 | .207 |
| 4 | 100 | 0 | 80 | 72.6 | 28.4 | 27.4 | 51.6 | .208 |
| 5 | 100 | 0 | 100 | 68.7 | 31.7 | 31.3 | 68.3 | .211 |
| 6 | 80 | 20 | 80 | 59.7 | 39.7 | 20.3 | 60.3 | .224 |
| 7 | 60 | 40 | 60 | 49.6 | 50.9 | 10.4 | 49.1 | .217 |
| 8 | 40 | 60 | 40 | 35.2 | 64.5 | 4.8 | 35.5 | .248 |

The second and third columns give the compositions of the solutions used; the fourth column gives the amounts of barium-saturated bentonite used; the fifth and sixth columns are the amounts of cadmium and barium found by analysis in the equilibrium solutions; the seventh and eighth columns give the composition of the solid phase calculated by difference; and the values in the last column are those of the equilibrium constant obtained by substitution in the equation

$$K' = \frac{Ba^{++}}{Cd^{++}} \times \frac{CdZ_2}{BaZ_2}$$

Since the ionic strength is constant throughout this series of experiments, the activity coefficients probably do not vary greatly, and they have been omitted in the calculations. These experiments were performed merely to show that the assumptions regarding the nature of the reaction are valid; and, judging by the nearly concordant values of $K'$, I think we are justified in assuming that this exchange reaction is accurately expressed by the equation

$$K = \frac{\gamma_{Ba^{++}}}{\gamma_{Cd^{++}}} \times \frac{Ba^{++}}{Ca^{++}}\text{ (in solution)} \times \frac{CdZ_2}{BaZ_2}\text{ (solid phase)}$$

A series of equilibria determinations were made at various concentra-

tions and at a temperature of 25°. The experimental data are presented in Table II.

TABLE II

EQUILIBRIA DATA FOR THE CADMIUM–BARIUM EXCHANGE REACTION AT VARIOUS CONCENTRATIONS, AND THE COMPARISON OF THE CALCULATED AND THE EXPERIMENTALLY DETERMINED VALUES OF THE RATIO

All concentrations expressed as milliequivalents per liter

| No. | Ionic strength | Final concentrations $Ba^{++}$ | $Cd^{++}$ | $BaZ_2$ | $CdZ_2$ | $K'$ | $K'_\infty/K'$ | $\frac{\gamma^3_{BaCl_2}}{\gamma^3_{CdCl_2}}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.0075 | 2.13 | 2.83 | 2.87 | 2.17 | 0.57 | 2.6 | 2.0 |
| 2 | .030 | 7.64 | 12.16 | 12.36 | 7.84 | .40 | 3.8 | 3.5 |
| 3 | .15 | 32.0 | 68.5 | 68.5 | 31.5 | .215 | 7.0 | 8.4 |
| 4 | .30 | 72.5 | 128 | 81.8 | 18.2 | .125 | 12 | 14 |
| 5 | 1.50 | 465 | 543 | 94.0 | 6 | .055 | 27 | 75 |

The values of $K'$ in the seventh column were calculated by substitution of the data into the equation

$$K' = \frac{Ba^{++}}{Cd^{++}}\text{ (in solution)} \times \frac{CdZ_2}{BaZ_2}\text{ (in solid phase)}$$

They were plotted against the square root of the ionic strength and extrapolated to infinite dilution. The data are meager and the extrapolation is not an exact one, but the value $K'_\infty = 1.5$ is probably not greatly in error. The next to last column of Table II contains the values of the ratio $\gamma_{Ba^{++}}/\gamma_{Cd^{++}}$ calculated from the values of $K'$ and the quantity $K'_\infty = 1.5$.

Making use of the published activity coefficient data for barium chloride and cadmium chloride and the hypothesis of Lewis and Randall, that in a dilute solution the activity coefficient of any ion depends solely on the total ionic strength, it is possible to calculate values for the ratio $\gamma_{Ba^{++}}/\gamma_{Cd^{++}}$. Using the notation of Lewis and Randall

$$\gamma_{Ba^{++}} = \frac{\gamma^3_{BaCl_2}}{\gamma^2_{Cl^-}} \text{ and } \gamma_{Cd^{++}} = \frac{\gamma^3_{CdCl_2}}{\gamma^2_{Cl^-}}$$

Dividing the first equation by the second we get

$$\frac{\gamma_{Ba^{++}}}{\gamma_{Cd^{++}}} = \frac{\gamma^3_{BaCl_2}}{\gamma^3_{CdCl_2}}$$

The last column of Table II contains the values of $\gamma_{Ba^{++}}/\gamma_{Cd^{++}}$ calculated from the activity coefficients of barium chloride and cadmium chloride interpolated from the values published by Scatchard and Tefft.[2]

It is undoubtedly highly presumptive to extend the hypothesis of Lewis and Randall to such high concentrations as occur in experiments 3, 4, and 5.

The agreement between the calculated and observed values is probably as good as can be expected when consideration is given to the assumptions

[2] G. Scatchard and R. F. Tefft, THIS JOURNAL, **52**, 2272 (1930).

underlying the calculated values and the analytical errors in the experimental determinations. The author is of the opinion that the cation-exchange reactions of bentonites offer an easy experimental way of determining relative activity coefficients with a fair degree of accuracy.


## Summary

A method for utilizing the cation-exchange reactions of bentonites for the determination of relative activity coefficients in mixed electrolytes has been presented. The method was applied experimentally to the barium–cadmium exchange reaction; the results are in fair agreement with those calculated from published data of the activity coefficients of barium chloride and cadmium chloride solutions.


RIVERSIDE, CALIFORNIA

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[CONTRIBUTION NO. 224 OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

# THE INTEGRAL HEATS OF DILUTION AND THE RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM CHLORIDE SOLUTIONS AT 25°

BY A. L. ROBINSON

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## I. Introduction

The accurate measurement of heats of dilution of strong electrolytes at concentrations below 0.1 *M* by Lange and his co-workers[1] and the successful extrapolation of these measurements to infinite dilution permit an evaluation of the relative partial molal heat contents of the components of such solutions in cases where measurements at higher concentrations have already been made. The dilution of very dilute aqueous solutions of strong electrolytes (in general below 0.1 *M*) evolves heat in every case so far studied, in agreement with the interionic attraction theory,[2] so that previous extrapolations of dilution measurements to infinite dilution, even when such measurements have been extended to concentrations of a few tenths molal, are often seriously in error. For example, Lewis and Randall[3] state that the dilution of a saturated solution of sodium chloride containing one mole of the salt with a very large amount of water absorbs 606 calories at 25° and that this agrees well with the value 598 calories calculated from partial molal heat contents. The measurements on dilute sodium chloride solutions presented here combined with the results of

[1] For a review of this work see Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931), which contains complete references.

[2] Lange and Meixner, *Physik. Z.*, **30**, 670 (1929).

[3] Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923, p. 95.

other investigators on more concentrated solutions give 483 calories for this heat effect, and permit the calculation of more accurate values of integral heats of dilution and of relative partial molal heat contents from saturation to infinite dilution. These latter values are important in the calculation of activity coefficients from freezing point data.

## II. Experimental

A differential adiabatic calorimeter, already described,[4,1] was employed. A thermopile with 1072 iron–constantan thermoelements was used to measure the heat effects attending the dilutions; with this thermopile and a Kipp and Zonen type Ze galvanometer the temperature changes produced by the dilutions, usually of the order of $10^{-4}$ degree, could be measured with an accuracy of $2 \times 10^{-7}$ degree.

The sodium chloride used was Merck's best preparation. Ordinary distilled water was used in making up the solutions and for dilution, as previous investigations had shown that further purification of the water was not necessary.

The dilution pipets, one in each half of the calorimeter, contained 25 cc. of solution, and each calorimeter half held 775 cc. of water or solution, not including the pipet contents. All details of manipulation and calculation were the same as in previous investigations.

TABLE I

HEATS OF DILUTION OF SODIUM CHLORIDE SOLUTIONS AT 25°

| Initial concn., mole/liter | Final concn., mole/liter | Individual measurements, $\Delta H$ calories/mole NaCl | | | | Average calories/mole NaCl |
|---|---|---|---|---|---|---|
| 0.1 | 0.00308 | −61.4 | −61.5 | | | −61.5 ± 0.1 |
| .1 | .00605 | −53.1 | −52.7 | | | −52.9 ± .2 |
| .05 | .00154 | −55.1 | −53.6 | −55.6 | −55.4 | −54.9 ± .6 |
| .05 | .00302 | −49.4 | −47.9 | −49.1 | −48.4 | −48.7 ± .4 |
| .025 | .000770 | −45.4 | −46.2 | −45.2 | | −45.6 ± .4 |
| .025 | .001515 | −39.1 | −40.7 | −39.9 | | −39.9 ± .6 |
| .0125 | .000385 | −32.8 | −32.2 | −34.4 | | −33.1 ± .9 |
| .0125 | .000754 | −30.8 | −29.2 | −31.6 | | −30.5 ± .9 |

The first two columns of Table I give the initial and final concentrations of a dilution, respectively. The third column of the table gives the heat effects of the individual measurements (negative values of $\Delta H$ indicate heat evolved) in this concentration interval calculated per mole of sodium chloride, and the fourth column gives the average of the individual measurements and the probable error, exclusive of any systematic errors. The reproducibility of the measurements is better than 2% except at the lowest concentrations, where there is an uncertainty of 3%.

## III. Discussion

The data of Table I are plotted against the square root of the molality (weight and volume concentrations differ inappreciably in this concentration range) in Fig. 1. Without the extrapolation to infinite dilution, only so-called "intermediate" heats of dilution could be read from the curve and only differences in the values of the relative partial molal heat

[4] Lange and Monheim, *Z. physik. Chem.*, **A149**, 51 (1930).

contents could be calculated. For example, $\Delta H$ here is an intermediate heat of dilution

$$\underset{}{\mathrm{NaCl}(0.09\ M)} + 770\mathrm{H_2O} \longrightarrow \underset{}{\mathrm{NaCl}(0.04\ M)}$$

$$\underset{}{\Delta H} = \underset{(0.04\ M)}{\bar{L}_2} + 1387\,\underset{(0.04\ M)}{\bar{L}_1} - \underset{(0.09\ M)}{\bar{L}_2} - 617\,\underset{(0.09\ M)}{\bar{L}_1}$$

When the final concentration of a dilution is zero, or when the measurements can be extrapolated to infinite dilution, $\Delta H$ becomes the integral heat of dilution, as

$$\underset{}{\mathrm{NaCl}(0.09\ M)} + (\infty - 617)\mathrm{H_2O} \longrightarrow \underset{}{\mathrm{NaCl}(0.0\ M)}$$

$$\underset{}{\Delta H} = \underset{(0.09\ M)}{-\bar{L}_2} - 617\,\underset{(0.09\ M)}{\bar{L}_1} = \Delta H_\infty$$

The measurements were extended to $3.85 \times 10^{-4}$ $M$, from which point an extrapolation to infinite dilution could be made with a probable error of less than one calorie, since below 0.12 $M$ the heats of dilution were

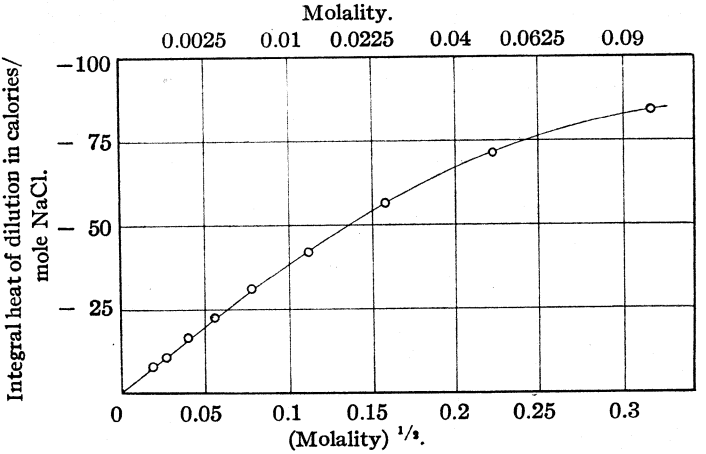


Fig. 1.—Integral heats of dilution of aqueous NaCl solutions at 25°.

found to be proportional to the square root of the molality within the experimental error of 2–3%. In this concentration region the integral heat of dilution per mole of sodium chloride is given by $\Delta H_\infty = -378\sqrt{m}$ calories.[5]

Lange and Messner[6] reported −23 calories as the heat of dilution, per mole of salt, of a 0.01 $M$ solution to 0.00138 $M$ at 25°. Interpolation of the results reported here gives −23.7 calories, in good agreement.

[5] The "limiting law" for the integral heat of dilution of 1–1 type salts, using Wyman's dielectric constant measurements [*Phys. Rev.*, **35**, 623 (1930)], and taking account of a correction pointed out by Scatchard [THIS JOURNAL, **53**, 2037 (1931)], is $\Delta H_\infty = -475\sqrt{m}$ calories per mole of salt. For a discussion of causes of deviation from the theoretical limit, see Lange and Robinson, Ref. 1.

[6] Lange and Messner, *Z. Elektrochem.*, **33**, 439 (1927).

Naudé[7] measured heats of dilution of sodium chloride in the concentration range 0.3–0.003 *M* at 18°. These values, when corrected to 25° using Rossini's tabulation of specific heats,[8] do not fit a smooth curve (see Fig. 2) and are evidently not of a high order of accuracy.

At higher concentrations Randall and Bisson[9] worked between 6.12 *M* (saturated solution) and 0.18 *M*, determining chiefly relative partial molal heat contents of water by direct measurement in this concentration range. Richards and Rowe[10] reported dilution measurements extending from 2.22 to 0.139 *M* at 20° and Pratt[11] measured intermediate heats of dilution between 2.22 and 0.25 *M* at 24 and 26°, as well as at other temperatures. Wüst and Lange[12] measured integral heats of solution of the salt to various concentrations down to 0.426 *M* at 25°, from which data intermediate heats of dilution are easily obtained.

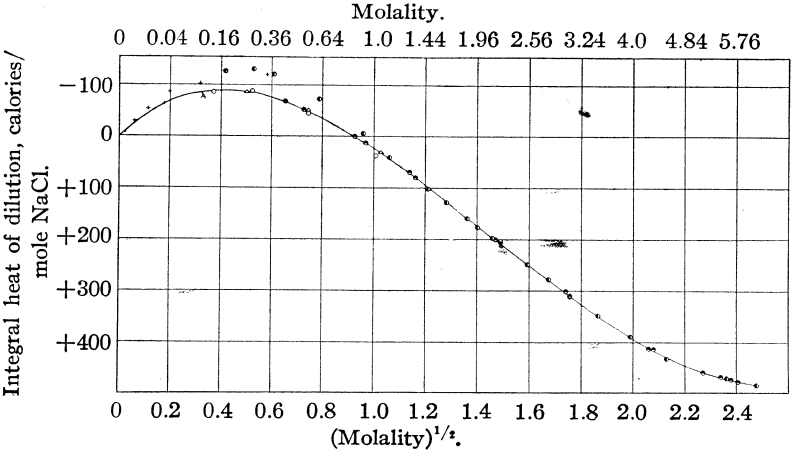


Fig. 2.—Integral heats of dilution of aqueous sodium chloride solutions at 25°: +, Naudé 18° (corrected to 25°); ○, Richards and Rowe, 20° (corrected to 25°); ◐, Randall and Bisson, 25°; △, Pratt (mean of 24° and 26°); ◓, Lange and Wüst; curve to A, these results.

To obtain integral heats of dilution for the complete concentration range up to saturation, and to calculate $\overline{L}_1$ and $\overline{L}_2$, our results (represented by the curve of Fig. 2 to A) were plotted on a large scale and fitted with the various measurements at higher concentrations. The data of Richards and Rowe were recalculated to 25°, using the temperature coefficient reported by them for possibly greater consistency, rather than the com-

[7] Naudé, *Z. Elektrochem.*, **33**, 532 (1927).
[8] Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).
[9] Randall and Bisson, THIS JOURNAL, **42**, 347 (1920).
[10] Richards and Rowe, *ibid.*, **43**, 770 (1921).
[11] Pratt, *J. Franklin Inst.*, **185**, 663 (1918).
[12] Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

piled specific heats of Rossini. The average of Pratt's values at 24 and 26° was used. The various measurements can be consistently combined except for the data obtained by Randall and Bisson in the more dilute region of the concentration range studied by them. The data of Lange and Wüst, Richards and Rowe and Pratt fall excellently on a smooth curve which can be joined to the measurements reported here with an uncertainty of only a few calories. Randall and Bisson added small amounts of water to definite amounts of solutions; the heat effects were very small (ranging from 0.01 to 3 calories per mole of water from 0.16 to 1.0 $M$ according to Table III) and certainly subject to a fairly large percentage error, while the measurements of the other investigators involved much larger heat effects and are probably relatively more accurate. Moreover, they agree very well with each other, particularly so considering the different experimental techniques. The smoothed curve has therefore been drawn without considering the more dilute measurements of Randall and Bisson. From 1 $M$ to saturation all the different sets of data agree very well. The measurements of Naudé are not of a high order of accuracy and have not been considered in drawing the portion of the curve to A.

Randall and Bisson reported that the further dilution of a 0.278 $M$ solution produced only a small heat effect and estimated 2 calories as the amount of heat *absorbed* in the dilution from 0.278 $M$ to infinite dilution. From the curve of Fig. 2 a value of 87 calories is read as the heat *evolved* in this process. It seems quite probable that extrapolations of heat of dilution measurements for other salts from concentrations where heat is still being absorbed by the dilution are also considerably in error.

In Table II are given the integral heats of dilution (the heat absorbed in diluting a solution containing one mole of sodium chloride at the concentration shown in the first column of the table to infinite dilution) as read from the smoothed curve of Fig. 2.

The most convenient and accurate method for obtaining values for $\bar{L}_1$ and $\bar{L}_2$ (the relative partial molal heat contents of water and sodium chloride, respectively) is that of Rossini.[13] From the definitions of $\bar{L}_1$ and $\bar{L}_2$ it can be shown that

$$\bar{L}_1 = \frac{m}{2(55.508)} \frac{d}{dm^{1/2}} (\Delta H_\infty) \text{ and } \bar{L}_2 = -\Delta H_\infty - \frac{m^{1/2}}{2} \frac{d}{dm^{1/2}} (\Delta H_\infty)$$

and from the plot of $\Delta H_\infty$ against $m^{1/2}$ in Fig. 2 values of the required slope are obtained and $\bar{L}_1$ and $\bar{L}_2$ are readily calculated. Table III gives the values of $\bar{L}_1$ and $\bar{L}_2$ so obtained and Fig. 3 shows a plot of these values against $m^{1/2}$.

The evolution of heat by the dilution of sodium chloride solutions below 0.2 $M$ produces a minimum in the values of $\bar{L}_1$ and a maximum in the values of $\bar{L}_2$ at about 0.15 $M$. The values of $\bar{L}_1$ do not rise gradually

[13] Rossini, *Bur. Standards J. Research*, **6**, 799 (1931).

TABLE II

INTEGRAL HEATS OF DILUTION OF AQUEOUS SODIUM CHLORIDE SOLUTIONS AT 25°

| Concentration, moles/1000 g. $H_2O$ | $\Delta H_\infty$ calories/mole NaCl |
|---|---|
| 0.0001 | − 3.5 |
| .001 | −11.9 |
| .005 | −27 |
| .01 | −38 |
| .05 | −70 |
| .1 | −83 |
| .2 | −90 |
| .4 | −72 |
| .6 | −42 |
| .8 | − 9 |
| 1.0 | 23 |
| 1.5 | 105 |
| 2.0 | 177 |
| 2.5 | 224 |
| 3.0 | 304 |
| 3.5 | 355 |
| 4.0 | 395 |
| 4.5 | 427 |
| 5.0 | 453 |
| 5.5 | 470 |
| 6.12 | 483 |

TABLE III

RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM CHLORIDE SOLUTIONS AT 25°[a]

| $m$, moles/1000 g. $H_2O$ | $L_1$, calories/mole | $L_2$, calories/mole |
|---|---|---|
| 0.0001 | −0.0000054 | 5.4 |
| .001 | − .00011 | 17.9 |
| .005 | − .0012 | 40.4 |
| .01 | − .0034 | 64 |
| .05 | − .0196 | 94 |
| .1 | − .0247 | 102 |
| .2 | − .0112 | 90 |
| .4 | .37 | 28 |
| .6 | 1.05 | − 48 |
| .8 | 1.95 | −120 |
| 1.0 | 2.98 | −188 |
| 1.5 | 6.39 | −343 |
| 2.0 | 10.2 | −466 |
| 2.5 | 13.7 | −556 |
| 3.0 | 17.5 | −626 |
| 3.5 | 20.3 | −671 |
| 4.0 | 21.2 | −688 |
| 4.5 | 20.9 | −683 |
| 5.0 | 19.6 | −656 |
| 5.5 | 15.8 | −620 |
| 6.12 | 9.2 | −570 |
| | $L_2$(s) = | −930[b] |

[a] Harned and Nims [THIS JOURNAL, **54**, 423 (1932)] report values for $\bar{L}_2$ referred to $\bar{L}_2$ (0.1 $M$) obtained from electromotive force measurements. In general the agreement with these results is only fair.

[b] Calculated from the data of Wüst and Lange.

from a value of zero, as previously reported,[14] but are negative up to 0.24 $M$, at which concentration $\bar{L}_1$ again has a zero value, and above this point increases gradually, reaching a maximum at about 4 $M$. $\bar{L}_2$ is also zero at infinite dilution by convention and has positive values up to about 0.45 $M$, at which concentration $\bar{L}_2$ again has a zero value, and above this point is negative, reaching a minimum at 4 $M$. This is of particular significance for the temperature coefficient of the activities of the sodium chloride and water since $\mathrm{d} \ln a_1/\mathrm{d}T = -\bar{L}_1/RT^2$, and the temperature coefficient of the mean activity coefficient of the salt is given by $\mathrm{d} \ln f_\pm/\mathrm{d}T = -\bar{L}_2/2RT^2$. At 25° $f_{NaCl}$ is decreasing with rising temperature below 0.45 $M$ and increasing above this concentration;[14a] the activity

[14] Randall and Bisson, THIS JOURNAL, **42**, 361 (1920).

[14a] The activity coefficient measurements of Harned and Nims [THIS JOURNAL, **54**, 423 (1932)], extending over the temperature range 0–40°, confirm this prediction qualitatively, although below 0.5 $M$ the trend in the values of the activity coefficients with temperature is probably not greater than the uncertainty in these values.

of the water is increasing with rising temperature up to 0.24 $M$ and decreasing above this concentration. This means that a plot of the activity coefficients of sodium chloride at various temperatures against the concentration will show intersections of the curves by each other. Since, in general, for the same concentration of salt, a more negative integral heat of dilution means a more positive value of $\overline{L}_2$ and since, in the cases

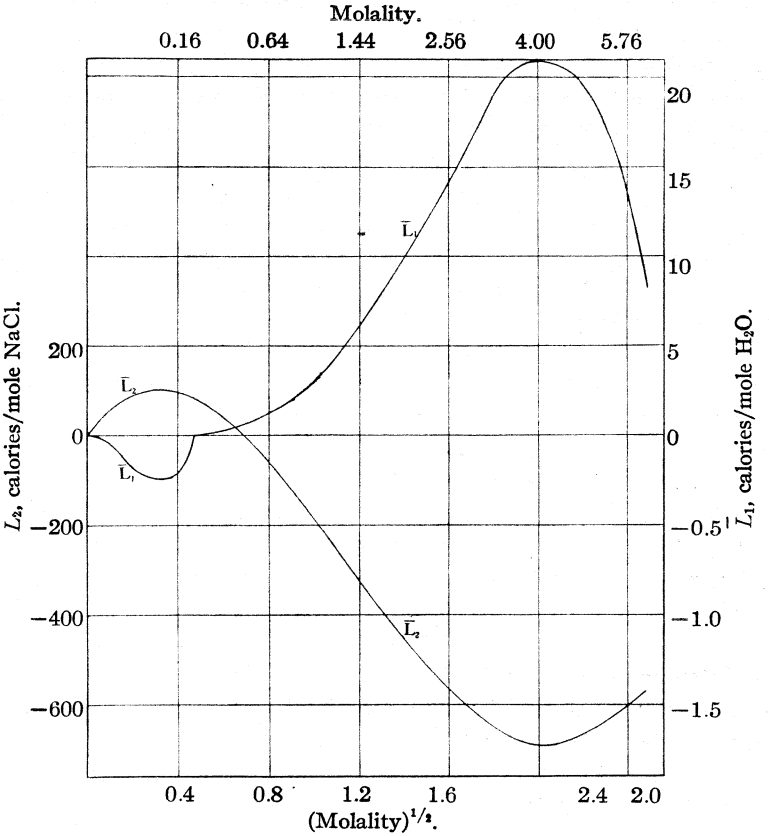


Fig. 3.—Relative partial molal heat contents in aqueous NaCl solutions at 25°

studied so far,[15] the integral heats of dilution become more negative with increasing temperature, it follows that the points of intersection of activity coefficient curves for the same salt at different temperatures will be found at higher concentrations at higher temperatures. For example, the plot of the activity coefficients of sodium chloride at 24, 25 and 26° against the concentration should show these three curves intersecting at about 0.45 $M$; below 0.45 $M$ $f_{24°}$ should have the highest value and $f_{26°}$ the smallest value, while above 0.45 $M$ the order of the curves should be

[15] Lange and Monheim, *Z. physik. Chem.*, **150A**, 349 (1931).

reversed. A similar plot of activity coefficients at 34, 35 and 36° should show the same reversal of order but the intersection should be at a higher concentration.

Curves representing $\bar{L}_1$ values for sodium nitrate, sodium chlorate and sodium bromate[16] plotted against $m^{1/2}$ show similar intersections below 0.1 $M$ as do similar curves for sodium sulfate, potassium sulfate, rubidium sulfate and cesium sulfate.[17] It follows that the $\bar{L}_2$ curves for these two series of salts must also intersect and therefore the relative order of their activity coefficients may show the same reversal that has been discussed above for sodium chloride. The possibility of such a reversal would of course depend upon the actual values of the activity coefficients, as determined by freezing point measurements for instance, as well as the actual $\bar{L}_2$ values. Accurate measurements of activity coefficients have not in general been extended to the same dilution as heat of dilution measurements, so that it is not possible to discuss the question quantitatively. It seems possible, however, that anomalies observed in a comparison of the order of the integral heats of dilution of series of salts with a common ion with the order of their activity coefficients[18] may be attributable to this cause. The extension of precise activity coefficient measurements to very small concentrations would be desirable in this connection.

The experimental portion of this work was carried out in the laboratory of Dr. E. Lange, in the Chemical Laboratory of the Bavarian Academy of Sciences, Division of Physical Chemistry, Munich, to whom the author is most grateful for the use of apparatus and for his kind friendship and helpful suggestions received during the course of many discussions.

## Summary

The intermediate heats of dilution of aqueous sodium chloride solutions have been measured in the concentration range 0.1–0.000385 $M$ at 25° and have been combined with the results of other investigators at higher concentrations to compute the integral heats of dilution and the relative partial molal heat contents of the components from infinite dilution to saturation.

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[16] Lange and Robinson, *Z. physik. Chem.*, **148A**, 146 (1930).

[17] Lange and Streeck, *ibid.*, **157A**, 23 (1931).

[18] Lange and Streeck, *Naturwissenschaften*, **19**, 359 (1931); Lange and Robinson, *Chem. Rev.*, 9, 89 (1931).

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

# METHYL RED AS AN ADSORPTION INDICATOR

BY GEORGE BATCHELDER AND VILLIERS W. MELOCHE

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The discovery of adsorption indicators by Fajans and Hassel[1] and the application of these indicators to the volumetric estimation of halides is well known. Although this work has been repeatedly verified and the number of available indicators increased, attempts to extend the principles involved to the quantitative determination of other ions have been comparatively rare. Investigations of this nature include the titration of lead with ferrocyanide[2] and the titration of mercurous ion with bromides[3] by Burstein, the estimation of phosphates and magnesium by Hahn and Meyer,[4] and more recently the titration of fluoride with cerous nitrate by the authors.[5,6]

In the titration of fluoride by means of cerous nitrate, either ampho magenta or methyl red was used and both were described as adsorption indicators. Subsequent experiments have demonstrated that the use of methyl red depends upon a principle which is different from the one usually ascribed to adsorption indicators. It is our purpose in the present paper to present evidence which will demonstrate that in precipitation titrations of fluoride and sulfate hydrolytic adsorption may take place with a resulting change of $P_H$, the function of the methyl red being that of an acid indicator.

**The Titration of Sulfate with Barium Chloride.**—In the titration of

[1] Fajans and Hassel, *Z. Elektrochem.*, **29**, 495–500 (1923).

[2] Burstein, *Z. anorg. allgem. Chem.*, **164**, 219–222 (1927).

[3] Burstein, *ibid.*, **168**, 325–326 (1928).

[4] Hahn and Meyer, *Ber.*, **60**, 975–977 (1927).

[5] Batchelder and Meloche, THIS JOURNAL, **53**, 2131–2136 (1931).

[6] For a review of the work on adsorption indicators the following bibliography may be consulted: K. Fajans and O. Hassel, *Z. Elektrochem.*, **29**, 495–500 (1923); R. Burstein, *Z. anorg. allgem. Chem.*, **164**, 219–222 (1927); R. Burstein, *ibid.*, **168**, 325–326 (1928); F. Hahn and H. Meyer, *Ber.*, **60**, 975–977 (1927); G. Batchelder and V. Meloche, THIS JOURNAL, **53**, 2131–2136 (1931); H. A. J. Pieters, *Chem. Weekblad*, **26**, 6–9 (1929); A. Frumkin, *Ber.*, **60**, 1816–1820 (1927); K. Fajans and K. von Beckerath, *Z. physik. Chem.*, **97**, 478–502 (1921); K. Fajans, *Naturwiss.*, **11**, 165 (1923); K. Fajans and W. Frankenburger, *Z. physik. Chem.*, **105**, 255–272 (1923); K. Fajans and H. Wolff, *Z. anorg. allgem. Chem.*, **137**, 221–245 (1924); O. Hassel, *Kolloid-Z.*, **34**, 304–307 (1924); W. Bottger and K. O. Schmitt, *Z. anorg. allgem. Chem.*, **137**, 246–248 (1924); O. Tomiček, *Časopis Českoslov. Lékárnictva*, **5**, 1–3 and 15–16 [*Chem. Zentr.*, **97**, 269–270 (1926)]; I. Kolthoff and L. van Berk, *Z. anal. Chem.*, **70**, 369–394 (1927); I. Kolthoff, *ibid.*, 395–397 (1927); I. Kolthoff, *ibid.*, **71**, 235–294 (1927); J. Hodakow, *Z. physik. Chem.*, **127**, 43–50 (1927); I. Kolthoff, W. Lauer and C. Sunde, THIS JOURNAL, **51**, 3273–3277 (1929); N. Rudenko, *J. Russ. Phys.-Chem. Soc.*, **62**, 505–548 (1930) (*Chem. Abst.*, **24**, 4233 (1930)); W. Hok, *Svensk. Farm. Tids.*, **34**, 161–167 and 185–190 (1930) (*Chem. Abst.*, **24**, 4899 (1930)).

fluoride with cerous nitrate, there was an unexpected interference of the sulfate ion. The nature of this interference led us to believe that adsorption principles might be used as the basis of a titration of sulfate by barium chloride. Stock solutions of barium chloride and sodium sulfate were prepared from C. P. reagents which had been purified by recrystallization and the strength of the solutions was determined by the customary gravimetric methods. Portions of the standard sodium sulfate solution were titrated according to the general procedure which follows.

**Procedure.**—An aliquot of the stock sulfate solution was placed in a beaker, heated to boiling[7] and titrated with standard barium chloride solution. Three to five drops of methyl red, 0.1% in alcohol, were used as indicator. At the end-point the solution changed from its initial yellow color to the red color corresponding to the acid range of the indicator. The visible particles of precipitate are not perceptibly colored. A few characteristic results are given in Table I.

TABLE I

STANDARD SOLUTION OF $BaCl_2$: 1 Cc. = 0.01786 G. OF $Na_2SO_4$

| $BaCl_2$, cc. | $Na_2SO_4$ added, g. | $Na_2SO_4$ found, g. | Initial vol., cc |
|---|---|---|---|
| 0.83 | 0.0150 | 0.0149 | 15 |
| .84 | .0150 | .0154 | 15 |
| .86 | .0150 | .0150 | 15 |
| .86 | .0150 | .0154 | 15 |
| 1.43 | .0250 | .0255 | 25 |
| 1.41 | .0250 | .0252 | 25 |
| 1.43 | .0250 | .0255 | 25 |
| 8.20 | .1500 | .1462 | 150 |
| 8.15 | .1500 | .1455 | 150 |

As will be noted from these results, the precision of this method proved to be only about 3%. The optimum conditions for the titration demanded the use of a relatively concentrated solution of barium chloride and this in turn necessitated the use of a microburet. The only conclusion to be drawn is that as a volumetric method for the estimation of sulfate, the above procedure has as yet little significance. However, the method is important in that it represents together with the previously mentioned more precise fluoride titration an example of a different application of adsorption principles to titrations.

**The Behavior of Methyl Red.**—The color change of adsorption indicators is usually described as being due to the deformation of the molecular structure of a dye ion when adsorbed upon an oppositely charged micelle. Thus, when silver ion is added to chloride ion in the presence of a small quantity of eosin, the halide is adsorbed upon the surface of the silver

[7] It has become evident that the advantage of boiling is mainly due to the adjustment of the $P_H$ by the removal of carbon dioxide. The same result is accomplished by passing hydrogen into the solution as was done in making potentiometric measurements.

chloride sol as soon as the latter develops, and particles of the type $(AgCl)_n$-$Cl^-$ are produced. However, when sufficient silver has been added to precipitate the last of the halide, the first excess of the silver is adsorbed to form particles of the type $(AgCl)_nAg^+$, and these particles in turn take up the negative eosin ion with a concomitant change of color. The reaction is reversible so that if enough chloride is now added to exceed the concentration of the silver, the latter (together with the eosin) is again removed from the micelle and the color change is reversed.

When neutral solutions of sodium fluoride were titrated with cerous nitrate using ampho magenta as the indicator, at the equivalence point the precipitate was colored and it seemed probable that the mechanism of the color change was quite similar to that described for the chloride titration. However, when methyl red was used as the indicator in the fluoride or sulfate titrations, the precipitated cerous fluoride or barium sulfate was not perceptibly colored at the equivalence point. The color change appeared in solution. Furthermore, the color change appeared to be quite similar to the usual acid color of methyl red.

The fact that with methyl red as the indicator the precipitate was not colored was further verified by use of the centrifuge. Standard barium chloride was added to an aliquot of sodium sulfate solution to which methyl red had been added. When the barium chloride was in excess and the color of the solution had changed from yellow to red, the mixture was centrifuged until the precipitated barium sulfate had thoroughly settled. In all cases the supernatant liquid was red and the precipitate was not colored. Finally, standard barium chloride was added to sodium sulfate solution in the absence of indicator. When the precipitate had been completely settled by means of the centrifuge, a few drops of methyl red were added to the surface of the supernatant liquid. A red color immediately appeared. These experiments were duplicated in the precipitation of cerium fluoride. When cerous nitrate was added in slight excess to a solution of sodium fluoride in the presence of methyl red and the resulting cerous fluoride separated by means of the centrifuge, the supernatant liquid was red and the precipitate was not colored.

From these experiments and the additional fact that the red color in the supernatant liquid could be discharged by the addition of alkali, it seemed evident that a change of $P_H$ occurred during the precipitation titrations mentioned. For this reason subsequent sulfate titrations were studied by means of the potentiometer, using the hydrogen electrode with the calomel half cell as reference electrode. The following curve is typical.

Attempts to make potentiometric studies of the fluoride titration were not successful. This was supposedly due to the formation of a coating of gelatinous cerous fluoride on the hydrogen electrode. Due to the conditions of the above sulfate titration good absolute $P_H$ values were not expected.

An examination of the curve suggests that, if a change of $P_H$ actually occurs as indicated, it should be possible to corroborate these results by means of properly selected indicators. The sulfate titration was therefore repeated using a variety of dyes. Of these dyes *p*-nitrophenol ($P_H$ 5.6 colorless–7.6 yellow), brom cresol purple (5.2 yellow–6.8 purple), and brom thymol blue (6.0 yellow to 7.6 blue) exhibited characteristic color changes in their respective ranges along the curve. Other indicators, whose color changes did not fall within the $P_H$ limits of the curve, did not give a change of color. This may be considered to indicate further a change of $P_H$ during titration.

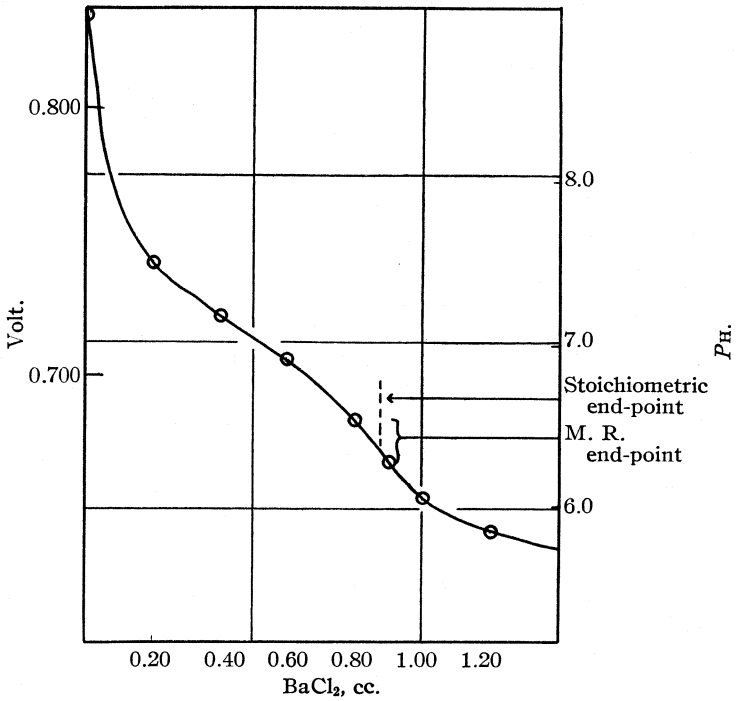


Fig. 1.—Titration of $Na_2SO_4$ with $BaCl_2$. Hydrogen electrode *vs.* satd. calomel.

**Hydrolytic Adsorption.**—It is difficult to explain the results given on any basis other than that of a change of the $P_H$ of the solution during titration. Similar phenomena have been known to colloid chemists for some time. Under proper conditions very appreciable quantities of acid may be produced in neutral solutions through the addition of activated charcoal. Some of the more recent studies of this phenomenon have been made by Bartell and Miller,[8] Frumkin[9] and Kolthoff and Kameda.[10]

[8] Bartell and Miller, THIS JOURNAL, **44**, 1866–1880 (1922).

[9] Frumkin, *Ber.*, **60**, 1816–1820 (1927).

[10] Kolthoff and Kameda, THIS JOURNAL, **51**, 2888–2900 (1929).

Earlier examinations of barium chloride and cerous nitrate solutions indicated that the results of the above titrations could not be due to ordinary hydrolysis but were probably due to hydrolytic adsorption. Assuming this to be the case, the following explanation seems reasonable. At the beginning of the sulfate titration particles of the type $(BaSO_4)_nSO_4^-$ are formed. When enough barium chloride has been added just to exceed the stoichiometric point the particle type becomes $(BaSO_4)_nBa^+$. Then, unlike the micelle of the chloride titration, the micelle in the sulfate titration adsorbs hydroxyl in preference to the negative dye ion. Likewise in the fluoride titration, at the beginning of the titration particles of the type $(CeF_3)_nF^-$ are formed and when the stoichiometric point is just exceeded the particle type becomes $(CeF_3)_nCe^+$. This latter micelle adsorbs hydroxyl rather than negative dye ion.

Whether this adsorption be preferential or the hydroxyl ion together with other negative ions is involved in a dynamic relationship between the micelles and the solution, the observed effect is the same as if hydroxyl ions had been removed from the solution.

The methyl red, then, in both the fluoride and the sulfate titration acts not in the usual capacity of adsorption indicators but rather as an indicator which detects the change of $P_H$ which takes place as a result of adsorption during the titrations.

It seems likely that the phenomenon described may be characteristic of other precipitation reactions. Further investigations along these lines are being undertaken at the present time.

## Summary

A precipitation titration of sulfate by means of barium chloride is described. Although this procedure is not satisfactory for the quantitative determination of sulfate, it has been used, together with a more precise fluoride titration, to illustrate a different application of methyl red to adsorption titrations.

Methyl red is described as an acid indicator which detects the change of $P_H$ at the end-point of two precipitation titrations. This change of $P_H$ was attributed to adsorption during the titrations.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# THE POTENTIOMETRIC DETERMINATION OF BROMINE, OCTAVALENT AND QUADRIVALENT OSMIUM IN HYDROBROMIC ACID SOLUTIONS. II

BY WILLIAM R. CROWELL

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## Introduction

In a study of the reaction between octavalent osmium and hydrobromic acid at 100° now in progress, it has been found that the products are quadrivalent osmium and bromine and that a state of equilibrium is reached. However, in concentrated hydrobromic acid solutions (about 8 *N*) the reaction goes to practical completion in the direction of formation of quadrivalent osmium and bromine, while in dilute acid solutions (about 0.1 *N*) the reaction goes to completion in the reverse direction. This behavior suggests (1) that octavalent osmium may be determined by heating it in a closed tube with concentrated hydrobromic acid and titrating the liberated bromine; (2) that quadrivalent osmium may be determined by heating it in a closed tube with a dilute hydrobromic acid solution containing excess bromine, titrating the bromine remaining and calculating the amount of osmium present from the amount of bromine used up. Because of the deeply colored solution formed in (1) and because of the presence of octavalent osmium in (2), potentiometric methods are found to be most satisfactory.

We have already shown that octavalent osmium may be determined with an accuracy of about 0.2% by direct potentiometric titration with hydrazine sulfate.[1] We have also shown that bromine may be determined in hydrobromic acid solutions of octavalent and quadrivalent osmium with an accuracy of about 0.5% by potentiometric titration with titanous sulfate.[2] The present paper presents results and describes how hydrazine sulfate may be used in an improved method of determining bromine in hydrobromic acid solutions of the two forms of osmium and shows how this method may be applied to indirect determinations of octavalent and quadrivalent osmium.

The value of hydrazine sulfate as a reducing agent in analytical work is well known. Bray and Cuy[3] have developed methods of standardization based on its oxidation by iodic acid, iodine, bromine and hypochlorous acid. Wellman has employed a potentiometric method for the determination of bromine in his study of the equilibrium between bivalent and

[1] Crowell and Kirschman, THIS JOURNAL, **51**, 175 (1929).

[2] Crowell and Kirschman, *ibid.*, **51**, 1695 (1929).

[3] Bray and Cuy, *ibid.*, **46**, 4 (1924).

quadrivalent palladium and chlorine in hydrochloric acid solution.[4] As a standard reagent, hydrazine sulfate is to be preferred over titanous salts because of its great stability in air and the ease with which it may be obtained in a pure form.

**Apparatus and Materials.**—The apparatus used was that employed in the potentiometric determination of octavalent osmium[5] and in the determination of bromine in the presence of octavalent and quadrivalent osmium.[2]

The hydrobromic acid free from bromine was obtained by distilling the 42–48% acid and retaining the middle portion.

The bromine solution was prepared from the C. P. reagent and was made 0.1 *N* in hydrobromic acid.

The osmium tetroxide solution was prepared by heating osmium metal in a tube in a current of oxygen at about 300° and absorbing the resulting osmium tetroxide in 0.4 *N* potassium hydroxide. The stock solutions, approximately 0.04 and 0.08 molal in $OsO_4$, were prepared by diluting this solution.

The hydrazine sulfate solution was prepared from the C. P. reagent and was standardized with recrystallized potassium iodate by the method of Bray and Cuy. The sodium thiosulfate was also standardized with potassium iodate.

The quadrivalent osmium solutions, approximately 0.04 and 0.08 molal in quadrivalent osmium, were prepared by heating known volumes of the stock osmium tetroxide solution in sealed tubes with enough concentrated hydrobromic acid to make the acid concentration about 8 normal, evaporating in a vacuum desiccator containing solid sodium hydroxide and sulfuric acid and diluting to the desired volume with 0.1 or 3.8 normal hydrobromic acid. Since there was an excess of potassium hydroxide in the stock osmium tetroxide solutions, the resulting product was really a solution of the potassium salt of quadrivalent osmium.

## Experimental Results

The experimental results are recorded in Tables I and II.

The data in Table I were obtained from results of potentiometric titrations of bromine in solutions of sulfuric acid, hydrobromic acid and of hydrobromic acid solutions of octavalent and quadrivalent osmium. In series 1, the bromine solution was forced by pressure into a pipet and run directly into an ice-cold solution of sulfuric acid containing slightly less than an equivalent amount of hydrazine sulfate. The titration was completed and the results obtained were compared with those obtained by the iodimetric method. In the table, the term "initial volume" means the volume before the addition of the hydrazine sulfate. In series 2 results of titrations of bromine in 0.2 *N* hydrobromic acid solution were compared with those also obtained potentiometrically when the bromine was added to water alone. In the latter case the acidity of the solution as determined by the amount of hydrobromic acid in the stock bromine solution was about 0.001 *N*. The purpose of these experiments was to determine whether or not there was an appreciable amount of bromine present in the hydrobromic acid used. In series 3 and 4 the procedure

[4] Wellman, THIS JOURNAL, **52**, 3 (1930).

[5] Crowell and Kirschman, *ibid.*, **51**, 175 (1929).

TABLE I

POTENTIOMETRIC TITRATION OF BROMINE SOLUTIONS WITH HYDRAZINE SULFATE

Volume of bromine solution taken, 1.996 cc. Volume of osmium solution taken, 1.00 cc. Initial volume, 240 cc. Concentration of hydrazine sulfate, 0.01017 *N*.

| Series | Acid and concn. | Osmium in titration beaker, millimole/liter $Os_4$ | $Os_8$ | $N_2H_6SO_4$ used, cc. | Bromine found, millieq./liter Potentiometric Stock soln. added to $H_2SO_4$, HBr and Os solns. | Stock soln. + water alone | Iodimetric stock soln. alone |
|---|---|---|---|---|---|---|---|
| 1 | 0.30 *N* $H_2SO_4$ | 0.00 | 0.00 | 31.82 | 162.2 | | 162.3 |
| | .30 *N* $H_2SO_4$ | .00 | .00 | 31.83 | 162.3 | | 162.3 |
| | .30 *N* $H_2SO_4$ | .00 | .00 | 31.78 | 162.0 | | 162.3 |
| 2 | .20 *N* HBr | .00 | .00 | 32.77 | 167.1 | 166.9 | |
| | .20 *N* HBr | .00 | .00 | 32.73 | 166.9 | 166.9 | |
| 3 | .10 *N* HBr | .00 | .15 | 32.32 | 164.8 | 164.0 | |
| | .10 *N* HBr | .00 | .15 | 32.37 | 165.1 | 164.0 | |
| | .075 *N* HBr | .00 | .15 | 32.10 | 163.6 | 164.0 | |
| | .083 *N* HBr | .00 | .15 | 32.02 | 163.2 | 163.3 | |
| 4 | .10 *N* HBr | .15 | .00 | 32.52 | 165.8 | 166.0 | |
| | .10 *N* HBr | .15 | .00 | 32.63 | 166.4 | 166.3 | |
| | .050 *N* HBr | .15 | .00 | 32.43 | 165.3 | 166.0 | |
| | .020 *N* HBr | .15 | .00 | 31.20 | 159.0 | 160.2 | |

TABLE II

THE POTENTIOMETRIC DETERMINATION OF OCTAVALENT AND QUADRIVALENT OSMIUM

Volume of osmium stock solutions used, 1.001 cc. Initial volume in titration beaker, 240 cc. Volume of constituents in reaction tubes, 10.0 cc.

| Series | Constituents in reaction tubes | 0.01017 *N* $N_2H_6SO_4$ required, cc. Titration of bromine liberated | Equivalent to bromine absorbed | Calculated concn. of osmium, millieq./liter From bromine titration | From titration of $OsO_4$ soln. used |
|---|---|---|---|---|---|
| 1 | $OsO_4$ + 8 *N* HBr | 30.80 | | 313.6 | 313.9 |
| | | 30.78 | | 313.4 | 313.9 |
| | | 30.83 | | 313.9 | 313.9 |
| 2 | $Os_4$ + 0.1 *N* HBr | | 31.00 | 315.6 | 315.1[a] |
| | + bromine | | 30.87 | 314.3 | 315.1[a] |
| | | | 30.92 | 314.8 | 315.1[a] |

[a] Result of titration of $OsO_4$ solution used to prepare the $Os_4$ solution.

was practically the same as that used in the analysis of the equilibrium mixtures consisting of bromine, hydrobromic acid and the two forms of osmium in relatively high concentrations. The bromine was added to a test-tube containing 8 cc. of an ice-cold solution 3.0 *N* in hydrobromic acid and approximately 0.004 molal in the osmium compound. In series 3 the osmium was in the form of $OsO_4$. The tube was sealed and then opened in ice water or dilute sodium hydroxide solution contained in a heavy-walled Pyrex beaker of 600 cc. capacity. The tip of the tube was broken against the side of the beaker beneath the surface of the solution, a small tube inserted into the opening and the contents forced out by gentle blowing. The solution was stirred just long enough to become thoroughly mixed, the hydrazine sulfate added and the titration com-

pleted. It was found that at this temperature there is an appreciable reaction between the hydrazine sulfate and the $OsO_4$, if the acidity is too high in any portion of the solution. By adding a small amount of dilute sodium hydroxide solution to the water in the titration beaker and stirring in the contents of the tube before the addition of hydrazine sulfate, the effect of the action of the acid on the $OsO_4$ is practically offset by the mechanical loss of bromine. In series 4, osmium was present in the quadrivalent form. The tubes were broken in a solution containing slightly less than an equivalent amount of hydrazine sulfate and, in the last two experiments, a small amount of base. After stirring, the titration was completed as in the other determinations. In these experiments the danger is in having the acidity so low that there is an appreciable reaction between the bromine and the quadrivalent osmium. The results obtained in both series 3 and 4 were compared with those obtained from potentiometric titrations of solutions formed by the addition of the bromine stock solution to water alone.

The data in Table II are results of determinations of octavalent and quadrivalent osmium. Series 1 are indirect determinations of octavalent osmium. A measured volume of the stock $OsO_4$ solution was sealed into a Pyrex tube containing an ice-cold solution of concentrated hydrobromic acid, the tube heated for one hour in the water-bath, cooled again, the contents broken into hydrazine sulfate solution and the titration of the bromine completed as in the previous experiments. The results obtained are compared with those found by direct potentiometric titration of the $OsO_4$ solution used. Series 2 are indirect determinations of quadrivalent osmium. A measured volume of stock bromine solution was sealed into a tube containing a known volume of stock $Os_4$ solution diluted with 0.1 *N* hydrobromic acid and chilled to near the freezing point. This tube was heated and the bromine left was titrated in the same manner as in the other experiments. The amount of bromine used up was determined, the concentration of the osmium calculated and the results compared with those obtained by direct potentiometric titration of the $OsO_4$ solution used to prepare the $Os_4$.

In the titration of the solutions in which only bromine and acid were present the fall in voltage at the end-point with the addition of one drop of reagent was 0.3–0.4 volt and was very rapid. In the presence of osmium the corresponding voltage drop was 0.2–0.3 volt and the rate of fall was much slower.

The results in Table I indicate that for a concentration of osmium as high as 0.15 millimole per liter there is no serious error in the titration of bromine by hydrazine sulfate in the presence of $OsO_4$ if the concentration of hydrobromic acid is no greater than about 0.08 *N*. In the case of quadrivalent osmium, the acidity should not be much lower than this.

In the determinations of octavalent and quadrivalent osmium the agreement between the results obtained by this method and those obtained by other methods is somewhat better than 0.2%.


## Summary

Potentiometric methods are described (1) for the determination of bromine in hydrobromic acid solutions of octavalent and quadrivalent osmium, (2) for the determination of octavalent osmium by titration of the bromine liberated when it is reduced by concentrated hydrobromic acid and (3) for the determination of quadrivalent osmium by determining the bromine required to oxidize it to the octavalent form when the reaction takes place in dilute hydrobromic acid. The reagent used is hydrazine sulfate. The accuracy of the method is about 0.2%.


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[CONTRIBUTION FROM THE DUNBAR LABORATORY OF HARVARD UNIVERSITY]

# THERMAL CONDUCTIVITY OF THE NORMAL PRIMARY SATURATED ALCOHOLS

BY M. DANILOFF

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Accurate quantitative information as to the variation of thermal conductivity of successive members of homologous series with molecular weight and with temperature is essential for the formulation of a defensible molecular theory of liquids. At the present time systematic data available on the subject under comparable conditions are scattered and incomplete.[1]

To supply this deficiency the thermal conductivity of seven normal primary saturated alcohols at 30, 75 and 100° and at atmospheric pressure have been determined by the writer by means of a special form of radial heat flow calorimeter comprising a thin cylindrical sheath of liquid.

The alcohols were obtained from the Eastman Kodak Chemical Company, Rochester, N. Y., and were of a very high order of purity as is shown by their range of boiling temperatures given in the summary of the results (Table I). Shipped in sealed bottles with ground-glass stoppers the samples were and remained perfectly colorless.

The apparatus used consisted chiefly of Bridgman's cylindrical calorimeter and is fully described elsewhere.[2]

[1] "International Critical Tables," 1929, Vol. V, p. 227, Table VI and p. 228, Tables X–XI; Landolt–Börnstein, "Physikalisch-Chemische Tabellen," 1931, Table 271, p. 1278; II Erg. Bd.; also ed. of 1927, I Erg. Bd.; Table 271, p. 715; Glazebrook's "Dictionary of Applied Physics," Article on "Thermal Conductivity," Vol. I, p. 429.

[2] P. W. Bridgman, "The Thermal Conductivity of Liquids under Pressure," *Proc. Am. Acad. Arts Sciences*, **59**, 7 (1923); J. F. Downie–Smith, "Thermal Conductivity of Liquids," *Ind. Eng. Chem.*, **22**, 1246 (1930).

Certain improvements were introduced by the writer, as, for example, the replacement of the manganin heating element by one of chromel of much higher resistance and of the same dimensions as previously. A special apparatus was constructed to ensure complete evacuation of the liquids from the calorimeter. This consisted essentially of a thick-walled cylinder into which the calorimeter could be inserted with a push fit. The whole was then immersed in an oil-bath and heated to approximately 120°, after which the cylinder with the calorimeter was placed under high vacuum (initial pressure less than 0.01 mm.) for eighteen hours in a thermally insulated flask. To ensure complete filling of the calorimeter by the more viscous alcohols, both the calorimeter and the liquids were preheated to approximately 80°. The calorimeter was then filled under high vacuum.

To prevent violent deflections of the galvanometer caused by Hertzian waves emanating from the contact of the thermostat, the latter was shunted by a condenser of high capacity. Close temperature regulation of the constant temperature bath at 100° proved difficult with the simple form of mercury-in-glass thermostat used in the original apparatus, but this difficulty was successfully overcome through the use of a toluene-mercury-in-glass thermostat.

In order to eliminate systematic errors due to possible electrical leaks each run consisted of four tests made with each of the four possible combinations of polarity of the thermocouple and heating element circuits.

Each value determined by the writer is a mean of a number of runs sufficiently large to reduce the probable error of the mean to 0.5% of the value of the mean of the means. The number of runs necessary to achieve this end varied from 8 to 15, but was in general in the neighborhood of 10. The standard deviation and the probable error of the mean were computed by the classical methods of statistics.

The results obtained are summarized in Table I and are also shown graphically in Figs. 1 and 2.

Methanol and *n*-butanol have not been tested by the writer since reliable values of their thermal conductivities at the desired temperatures had already been published by a previous investigator.[2]

Figure 1 in which the thermal conductivities of the alcohols at different temperatures have been plotted against molecular weight shows the existence of a marked minimum of thermal conductivity for *n*-hexyl alcohol. This is not an isolated instance; in fact, maxima and minima of physical properties in homologous series for the member containing six carbon atoms (or for members closely adjacent to the latter) are of not infrequent occurrence. The following examples may be cited: the melting points at atmospheric pressure of saturated alcohols, *o*-toluidines, *p*-bromo-anilines and *p*-bromonaphthalenes; the ionization constants of the carboxylic acids have a minimum around the six carbon atom member. The molecular

TABLE I

THERMAL CONDUCTIVITIES IN GRAM-CAL. PER SEC. PER SQ. CM. PER °C. PER CM. × $10^6$ OF NORMAL PRIMARY SATURATED ALCOHOLS AT 30, 75 AND 100°C. AND AT ATMOSPHERIC PRESSURE

| Alcohol | Range of boiling temp., °C. | Number of carbon atoms | Molecular weight | Thermal conductivity × $10^6$ at 30° | 75° | 100° |
|---|---|---|---|---|---|---|
| Methyl | | 1 | 32.04 | 503[a] | 492[b] | ... |
| Ethyl[c] | | 2 | 46.05 | 433 | 416[b] | ... |
| *n*-Propyl | 96–98[d] | 3 | 60.08 | 409 | 393 | ... |
| *n*-Butyl | | 4 | 74.10 | 394[a] | 382[a] | ... |
| *n*-Amyl | 136–139[d] | 5 | 88.11 | 388 | 375 | 368 |
| *n*-Hexyl | 155–157[d] | 6 | 102.15 | 386 | 374 | 368 |
| *n*-Heptyl | 154–156[d] | 7 | 116.17 | 389 | 376 | 372 |
| *n*-Octyl | 191–194[d] | 8 | 130.18 | 398 | 387 | 375 |
| *n*-Nonyl | 97–99 (14 mm.) | 9 | 144.21 | 401 | 391 | 382 |

[a] Value obtained by P. W. Bridgman.[2] [b] Extrapolated value obtained from P. W. Bridgman.[2] [c] The sample of ethyl alcohol used contained 99.8% of absolute ethanol, the impurities consisting chiefly of water. [d] At atmospheric pressure.

optical rotation of the methyl esters of dibasic fatty acids shows three relative maxima for the members containing 3, 6 and 9 carbon atoms.

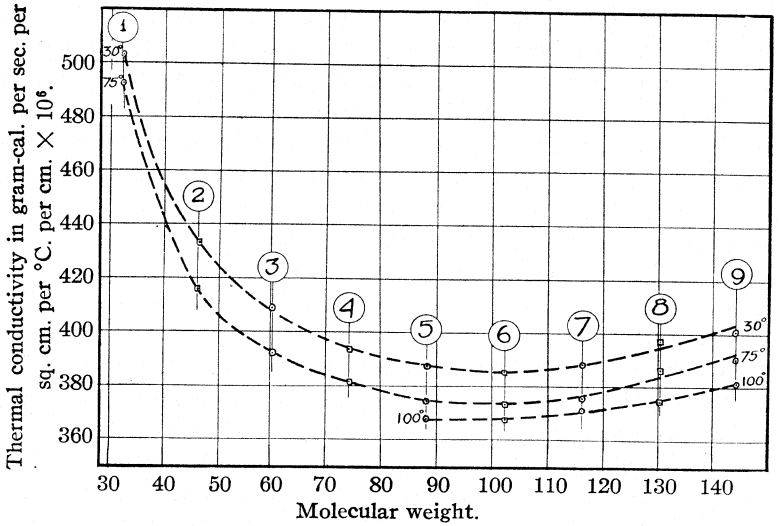


Fig. 1.—Variation of thermal conductivity of normal primary saturated alcohols with molecular weight at 30, 75 and 100° and at atmospheric pressure. The figures in the circles indicate the number of carbon atoms in the alcohol.

It has been suggested that a possible explanation of this behavior lies in the known fact that the angles between the bonds of the carbon atoms are equal to 120°, and, therefore, that the spirals formed by the open-chain hydrocarbons could be expected to exhibit singular spatial relations when

the number of carbon atoms present in the chain is a multiple of three. Recent x-ray studies seem to point in the same direction.

An examination of the curves of Fig. 1 as well as a comparison between the thermal conductivities of isomeric alcohols leads to the conclusion that the thermal conductivities of saturated alcohols do not possess the property of additivity.

In many homologous series the physical properties of the member of lowest molecular weight are often exceptional, but in the series under consideration this cannot be said to be true, for the value for methyl alcohol, although relatively high, fits the general curves well. Also the members with odd and even numbers of carbon atoms are seen to possess values of thermal conductivity lying on a common curve.

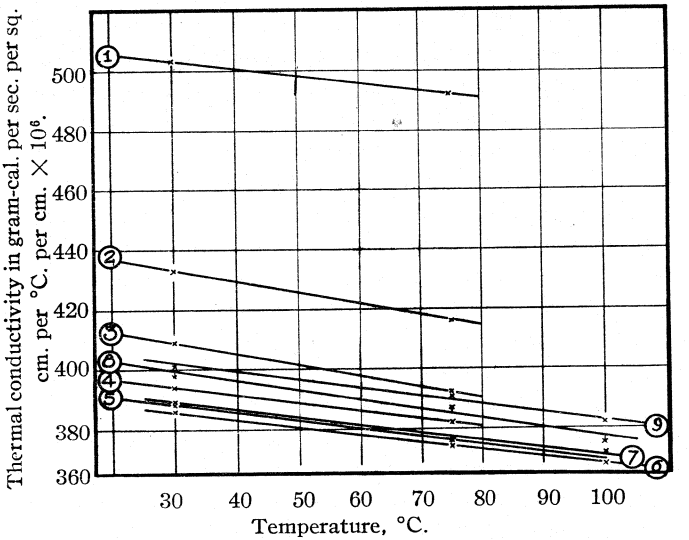


Fig. 2.—Variation with temperature at atmospheric pressure of the thermal conductivity of saturated normal primary alcohols. The figures in the circles indicate the number of carbon atoms in the alcohols.

Figure 2 in which the thermal conductivities of the different alcohols have been plotted against temperature shows that normal saturated alcohols have a negative temperature coefficient of thermal conductivity and that the variation of thermal conductivity with temperature is very nearly linear. The temperature coefficient has substantially the same value for all the alcohols investigated. The curve for normal butanol was fitted to values taken from P. W. Bridgman[2] and agrees well with the writer's own curves. This is the more significant because an error in a value of thermal conductivity may cause a very much larger error in the temperature coefficient of thermal conductivity.

The writer is indebted to Professor P. W. Bridgman of Harvard College for the loan of his cylindrical calorimeter and to Mr. J. F. Downie-Smith, Assistant in draughting at the Harvard Engineering School, for the use of his equipment.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 686]

# CONCERNING THE ACIDITY OF SOLUTIONS OF SODIUM METAPHOSPHATES. APPROXIMATE STRENGTH OF MONOMETAPHOSPHORIC ACID. VI

BY SAMUEL J. KIEHL AND THOMAS M. HILL

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The acidity of solutions of sodium monometaphosphate, which was prepared by the method of Beans and one of us,[1] was found to diminish when it was recrystallized several times from water. This feeble acid reaction of such solutions of the fused product obtained by heating monosodium orthophosphate has been known since Graham's[2] memorable work. In his report this statement is found concerning the "fused insoluble variety:" "When the preceding insoluble variety, or the biphosphate in any condition, is heated in a platinum crucible to low redness, it undergoes fusion, and on cooling presents itself as a transparent glass, which deliquesces in a damp atmosphere and is highly soluble in water. *But the fused salt has undergone a most extraordinary and permanent change of properties.* The solution has a very feeble acid reaction when compared with crystallized biphosphate." This salt referred to by Graham is classed by J. W. Mellor[3] in a summary as a hexametaphosphate, under which he gives the property of acidity referred to above. G. Tammann[4] believed that Graham's salt was a mixture of three isomeric hexametaphosphates.

The significant fact that the salt prepared by us diminished in acidity when it was recrystallized several times from water indicated that the substance responsible for the acidity was capable of separation and that it existed as an impurity. The source and identity of the acid impurity was therefore sought.

Graham[2] also prepared disodium dihydrogen pyrophosphate by carefully heating monosodium orthophosphate and under properties stated that the solution was acid when no monosodium orthophosphate, detectable by silver nitrate, remained. He found also that the solutions became

[1] Beans and Kiehl, THIS JOURNAL, **49**, 1878 (1927).

[2] Graham, *Phil. Trans.*, **123**, 253 (1833).

[3] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, 1922, p. 870.

[4] Tammann, *J. prakt. Chem.*, [2] **45**, 463 (1892).

very acid as the white silver pyrophosphate was precipitated. In consideration of the similar methods of preparation it therefore is not improbable that the acidity of the product of his fused "insoluble variety" was due to the presence of the disodium dihydrogen pyrophosphate. Furthermore, if it is due to the presence of the above pyrophosphate, the "insoluble variety" must also contain it.

Accordingly, some of Graham's "insoluble variety" was prepared from carefully purified monosodium orthophosphate. The substance, in portions, was ground in an agate mortar with distilled water until a large quantity came in contact with the water. From solutions so prepared positive tests were obtained repeatedly for pyrophosphate by the following method of detection developed by Dr. H. P. Coats and one of us:[5] "A thirty-two hundredths molar zinc acetate solution in the presence of one-eighth its volume of glacial acetic acid is sufficiently sensitive to detect six ten-thousandths molar pyrophosphate in the presence of tenth molar ortho- and tenth molar monometaphosphate." Solutions of the sodium monometaphosphate prepared by us also gave positive tests for pyrophosphate.

In addition to the above precipitaton tests for pyrophosphate the changes in acidity of solutions of our recrystallized monometaphosphate were followed by Clark's indicators and color scale. A tenth molar solution of the metaphosphate prepared by crystallization at 450° from fusion gave a hydrogen-ion concentration of $2.4 \times 10^{-5}$. After two crystallizations the hydrogen-ion concentration dropped to $2.5 \times 10^{-6}$. A third crystallization produced no perceptible change. A fourth crystallization, however, was carried out fractionally. The first portion gave a hydrogen-ion concentration of $1.6 \times 10^{-6}$ and the second, $6.3 \times 10^{-7}$ moles per liter in tenth molar solutions. The purifications and measurements were made in conductivity water. The last solution was considered essentially free from pyrophosphate.

To ascertain if heat treatment could cause a change in hydrogen-ion concentration, the following experiments were performed and the hydrogen-ion concentration of tenth molar solutions of substances treated as described in the table was determined. The thrice crystallized sodium monometaphosphate whose tenth molar solution gave a hydrogen-ion concentration of $2.5 \times 10^{-6}$ moles per liter was used in a comparative way. Measurements were made in conductivity water at 20°.

The results in the table indicate that the heat treatments have produced no significant changes in the acidic nature of the materials. The cause of the acidity of solutions of the various metaphosphates seems not to be due to the formation of polymeric forms whose formation might occur under conditions provided in the above experiments.

[5] Kiehl and Coats, THIS JOURNAL, **49**, 2180 (1927).

TABLE I

EXPERIMENTAL DATA

| Expt. | Material treated | Treatment | $C_{H^+} \times 10^6$ |
|---|---|---|---|
| 1 | $NaH_2PO_4$ | Heated carefully, fused and crystd. at 450° | 24.0 |
| 2 | $NaH_2PO_4$ | Heated carefully, held in fused state 14 hours and then crystd. at 450° | 24.0 |
| 3 | $NaH_2PO_4$ | Heated carefully to 400° until meta was formed without fusion | 24.0 |
| 4 | $NaH_2PO_4$ | Heated carefully to fusion and quenched | 40.0 |
| 5 | Metaphosphate prepared in Expt. 1 | Recrystallized twice | 2.5 |
| 6 | Purified salt of Expt. 5 | Held 18 hours 450° | 1.6 |
| 7 | Purified salt of Expt. 5 | Fused and quenched | 2.5 |

The feeble acid nature of the solutions is doubtless due to disodium dihydrogen pyrophosphate which is formed during the preparation. A study of the dissociation pressure of monosodium orthophosphate was made by Wallace[6] and one of us in which the dissociation pressure of monosodium orthophosphate to disodium dihydrogen pyrophosphate was found to be much below that of disodium dihydrogen pyrophosphate to metaphosphate at lower temperatures. The formation of disodium dihydrogen pyrophosphate would no doubt occur in considerable amount in the beginning and it would be retained in the molten mass in spite of the prolonged heating.

From tests outlined above it seems that the acidity of solutions of "Graham's salt" and other sodium metaphosphate prepared from monosodium orthophosphate by heating without recrystallization from water is due to disodium dihydrogen pyrophosphate.

**Approximate Strength of Monometaphosphoric Acid.**—If it is logical and sound to consider the acidity or alkalinity resulting from hydrolysis of an aqueous solution of a normal salt as a measure of the strength of the acid or base, it is of interest to note the relative position assumed by monometaphosphoric acid when hydrogen-ion concentration measurements in solutions of its sodium and ammonium salts are compared to the position determined for other acids by similar measurements in solutions of their carefully purified sodium and ammonium salts. By use of indicators and Clark and Lubs' color chart, the hydrogen-ion concentration in moles per liter for tenth molar solutions of the salts are:[7] ammonium monometaphosphate $1.6 \times 10^{-6}$, sodium monometaphosphate $6.3 \times 10^{-7}$, ammonium chloride $1.6 \times 10^{-5}$, sodium chloride, $1 \times 10^{-5}$, ammonium nitrate $6 \times 10^{-6}$ and sodium nitrate $4 \times 10^{-6}$. The hydrogen-ion concentrations of solutions of the monometaphosphates are much lower than those of the two well-known strong acids. When it is compared, moreover,

[6] Kiehl and Wallace, THIS JOURNAL, **49**, 375 (1927).

[7] Kiehl and Hill, *ibid.*, **49**, 123 (1927).

with sodium acetate, whose hydrogen-ion concentration is $3.2 \times 10^{-8}$ in a tenth molar solution, it would assume a position much nearer the strong nitric acid than the weak acetic acid. Such an approximation would place it near sulfuric acid but below it.


## Summary

1. The presence of disodium dihydrogen pyrophosphate is given as an explanation for the acidity of solutions of "Graham's salt" and solutions of other sodium metaphosphates prepared by heating monosodium orthophosphate when they are not purified by repeated crystallizations from water.

2. The monometaphosphoric acid is near but below sulfuric acid with respect to its activity.


NEW YORK CITY

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

# CALCIUM NITRATE. III. HEATS OF HYDRATION AND OF SOLUTION OF THE BINARY SYSTEM CALCIUM NITRATE–WATER

BY WARREN W. EWING, ALFRED N. ROGERS, JOHN Z. MILLER AND EDWARD MCGOVERN

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By means of well-known thermodynamic principles, heats of hydration of salts can be calculated from vapor pressure–temperature data. The system calcium nitrate–water lends itself admirably to an investigation of these relationships since the salt crystallizes from water in four forms—the tetrahydrate, the trihydrate, the dihydrate and the anhydride, according to the concentration of the solution and other conditions. In a previous article,[1] a temperature–composition diagram was presented showing that each of these crystalline forms can exist in a metastable equilibrium with what is ordinarily called a supersaturated solution. In reality they are saturated solutions of the metastable crystals. In a second article,[2] temperature–vapor pressure data for the mixture of crystals of this system were presented. It was shown that equilibrium vapor pressures could be measured not only for the stable eutectic mixtures tetrahydrate–trihydrate, trihydrate–dihydrate, and dihydrate–anhydride, but also for the metastable eutectic mixtures tetrahydrate–dihydrate and tetrahydrate–anhydride.

Fragmentary data are given in "International Critical Tables" for the experimental heats of this system. In order to compare the heats calculated from vapor pressure measurements with experimental data, it seemed advisable to make accurate heat measurements for the reactions

[1] Ewing, Krey, Law and Lang, THIS JOURNAL, **49**, 1958 (1927).

[2] Ewing, *ibid.*, **49**, 1963 (1927).

involved, employing modern calorimetric methods. The heats of solution of the anhydride, the dihydrate, the trihydrate and the tetrahydrate have been measured. From these data, one can calculate the heat of hydration from any lower hydrate to any higher one.

Similar measurements have been made also for the binary system strontium nitrate–water as vapor pressure–temperature data for this system are now being obtained in this Laboratory.

The general procedure for measuring the heats of solution was to introduce the solute into water and measure the temperature change under adiabatic conditions. This temperature change was then reproduced by means of electrical energy, and the electrical energy necessary to reproduce these changes was equated to the heat of solution. If due precautions are taken to have all changes in the system the same during the electric heating and the chemical heating, this method practically eliminates corrections for heats due to stirring, evaporation, electrical stray fields due to the bath heating current, etc. Precautions were taken to minimize any effect which might cause error, however, in order to make the changes which must be compensated for as small as possible.

## Experimental

The adiabatic calorimeter used in making these heat measurements contains features described by Cohen, Moesveld and Helderman,[3] Daniels,[4] and others. Its details are illustrated in Fig. 1.

The outer can was made of copper. The heavy copper cover was attached to the can by means of the ground brass joint, G, which was well coated with rubber desiccator grease; after closing, it was sealed with universal wax. No sign of leakage was ever detected. A, B and C are copper chimneys lined with hard rubber tubes. Also the stems of the breaking devices and of the heater-stirrer were made of hard rubber. Four chimneys are not shown in the diagram. One of these admitted the thermometer; the other three, additional breaking devices. The thermometer was a mercury-in-glass instrument graduated in 0.01° from 18 to 28°. It was standardized at the Bureau of Standards. The gold-plated calorimeter can had a capacity of 1300 ml. The heating element in the heater-stirrer was made of constantan wire. It was wound on mica and housed in the thin copper vanes of the stirrer. The whole stirrer was carefully gold plated and then coated with a waterproof lacquer. The heating element was connected to the potentiometer and to an 8-volt, 320 ampere-hour lead storage battery by means of concentric mercury wells in the hard rubber disk, D.

The solute was introduced by means of small glass bulbs of 7-ml. capacity. These bulbs were closed either by fusion or by means of universal wax according to the nature of the contents. If wax was used the bulbs were always tested for leakage before using. The contents of the bulbs were introduced into the solvent by shattering the bulbs with the rod in the breaking device. The use of four small bulbs rather than one large one made possible a more gradual temperature change and, consequently, more accurate adiabatic control.

[3] Cohen, Moesveld and Helderman, *Z. physik. Chem.*, **112**, 141 (1924).

[4] Daniels, THIS JOURNAL, **38**, 1473 (1916).

The surrounding bath was heated by means of a 110-volt alternating current passing through the dilute copper sulfate solution. This gave uniform heating and avoided time lag. The bath was cooled by passing water through a copper cooling coil. E was a by-pass. The surface of the bath was covered with a one centimeter layer of paraffin wax.

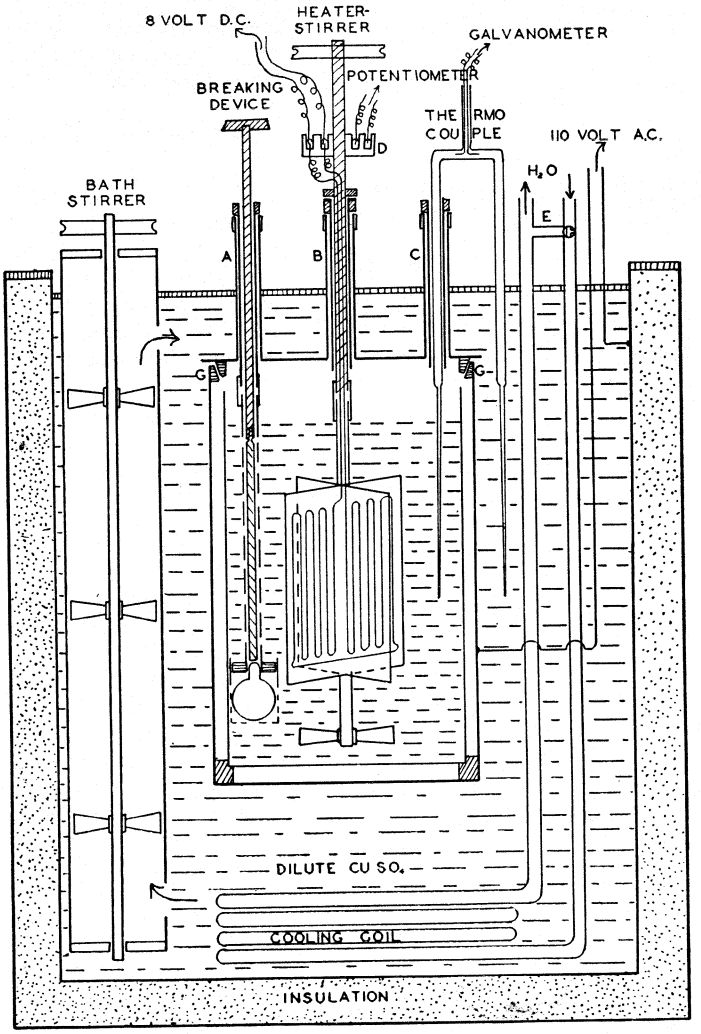


Fig. 1.

Adiabatic conditions were maintained between the calorimeter and the bath by the automatic control pictured at the right side of Fig. 2. The current from the photo-electric cell was amplified by means of a vacuum tube before passing through the sensitive relay. This arrangement kept the temperature difference between the bath and the calorimeter within 0.01°, even when the temperature was changing rapidly because of heat of reaction. Control tests showed that this was sufficiently accurate for this

calorimeter. The electrical power input into the calorimeter was measured by means of the hook-up diagrammed at the left of Fig. 2. The time of heating was measured to one-fifth of a second by means of an accurate stop watch. The magnitude of the current was determined by measuring the potential drop across the standard resistance. The energy data were calculated from the current and the resistance of the heater, assuming that the latter remained constant.

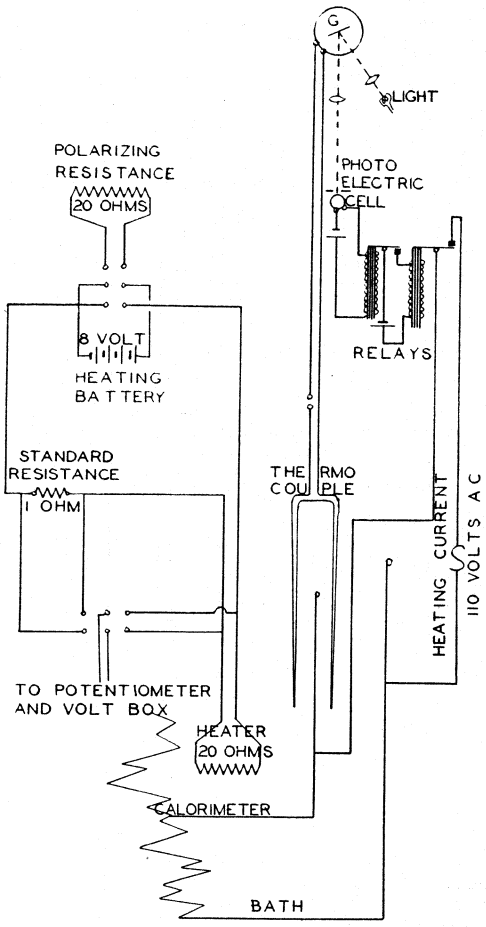


Fig. 2.

## Preparation of Materials

The calcium nitrate and the strontium nitrate were purified by recrystallizing the C. P. salts in the form of tetrahydrates, the calcium nitrate three times and the strontium nitrate twice. The temperature–composition and the temperature–vapor pressure diagrams for these hydrates enable one to choose the correct conditions for preparing the various hydrates. Similar data on strontium nitrate are being accumulated in this Laboratory. Calcium nitrate tetrahydrate was crystallized from solution at room temperature and dried over 60% sulfuric acid. Calcium nitrate trihydrate was prepared by melting together the stoichiometric ratios of the tetrahydrate and the anhydride. The crystallization of this melt at a constant temperature, 51.1°, gave assurance that the crystals formed were trihydrate. They were stored in a desiccator with tetrahydrate to constant weight. Calcium nitrate dihydrate was crystallized by evaporating a solution very slowly at 51° in a constant temperature bath. The large crystals formed were dried on filter paper and finally stored in a desiccator over the anhydride. Calcium nitrate anhydride crystals were dried to constant weight over phosphorus pentoxide.

Strontium nitrate tetrahydrate crystals were crystallized from solution at room temperature, which is a few degrees below the transition temperature. The drying of this salt gave considerable trouble. The tetrahydrate–anhydride mixture has a high vapor pressure; consequently, the tetrahydrate effloresces in air at ordinary humidities. The traces of anhydride formed tend to go into saturated solution of anhydride rather than back to tetrahydrate on taking up moisture. The difficulty was finally overcome by filtering and drying the crystals with filter paper in a constant humidity chamber at the vapor pressure of the saturated solution. These crystals when stored in a desiccator over a mixture of anhydride–tetrahydrate proved to be satisfactory. Strontium

nitrate anhydride was prepared by drying over phosphorus pentoxide. In all cases the crystals were analyzed for water content.

## Results

The data are given in Table I. Column 2 shows the weight of solute which was contained in the four small glass bulbs for each experiment.

TABLE I

HEATS OF SOLUTION OF THE SALTS IN 1000 GRAMS OF WATER

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| Salt | Wt. of salt | Final concn., moles anhyd. per 1000 g. $H_2O$ | $\Delta H$ joules/mole | Deviation from mean, % |
| $Ca(NO_3)_2$ | 17.1846 | 0.1047 | −18,450 | +0.5 |
| | 20.2548 | .1234 | −18,620 | +1.5 |
| | 20.2359 | .1233 | −18,200 | −0.8 |
| | 20.3075 | .1238 | −18,380 | +0.2 |
| | 14.8316 | .0902 | −18,740 | +2.2 |
| | 15.0102 | .0914 | −19,300 | +5.5 |
| | 16.3508 | .0997 | −17,830 | −2.9 |
| | 16.0554 | .0978 | −17,880 | −2.6 |
| | 16.7814 | .1023 | −17,770 | −3.2 |
| | | | Average, −18,350 | |
| | | | I. C. T., −16,500 | |
| $Ca(NO_3)_2 \cdot 2H_2O$ | 25.6322 | 0.1276 | +12,750 | +0.7 |
| | 25.6432 | .1277 | +12,580 | −0.7 |
| | 25.5576 | .1273 | +12,670 | 0.0 |
| | | | Average, +12,670 | |
| | | | I. C. T., + 8,600 | |
| $Ca(NO_3)_2 \cdot 3H_2O$ | 20.1590 | 0.0919 | +16,280 | −4.5 |
| | 20.0377 | .0914 | +16,950 | −0.6 |
| | 20.1371 | .0918 | +17,910 | +5.1 |
| | | | Average, +17,050 | |
| | | | I. C. T., +22,000 | |
| $Ca(NO_3)_2 \cdot 4H_2O$ | 20.3652 | 0.0857 | +33,090 | −0.2 |
| | 20.3519 | .0856 | +33,150 | −0.1 |
| | 20.3525 | .0856 | +33,410 | +0.7 |
| | 19.5599 | .0823 | +33,190 | +0.1 |
| | 20.1012 | .0846 | +32,910 | −0.8 |
| | 20.4306 | .0860 | +33,260 | +0.3 |
| | | | Average, +33,170 | |
| | | | I. C. T., +30,300 | |
| $Sr(NO_3)_2$ | 30.6130 | 0.1446 | +17,980 | −0.4 |
| | 30.7677 | .1453 | +18,260 | +1.2 |
| | 31.2931 | .1478 | +17,890 | −0.8 |
| | | | Average, +18,040 | |
| | | | I. C. T., +18,900 | |
| $Sr(NO_3)_2 \cdot 4H_2O$ | 24.9957 | 0.0881 | −52,490 | +1.0 |
| | 23.9139 | .0843 | −51,410 | −1.0 |
| | | | Average, −51,950 | |
| | | | I. C. T., −51,500 | |

When these weights of salt were dissolved in the 1000 g. of water in the calorimeter, the concentrations in column 3 were obtained. These are expressed in moles of anhydride per 1000 g. of water. These concentrations vary from 0.08 to 0.13 molal. The changes in heat content, $\Delta H$, per mole of solute are tabulated in column 4.

Lange and Streeck[5] find for the heats of dilution of calcium nitrate and of strontium nitrate solutions from 0.1 *m* to infinite dilution $\Delta H = -900$ joules and $\Delta H = -500$ joules, respectively. These values added to the average heats of solution in Table I give the integral heats of solution when the salts are dissolved in an infinite quantity of water. These integral heats of solution are presented in Table II.

Experimental heats of hydration with liquid water, Table III, column 2, are obtained from these heats of solution. The method of summation may be illustrated by taking the trihydrate–tetrahydrate reaction as an example

(1) $Ca(NO_3)_2 \cdot 3H_2O(s) + aq \longrightarrow Ca(NO_3)_2(aq) + 3H_2O(l)$; $\Delta H_1 = +16{,}150$ j.
(2) $Ca(NO_3)_2 \cdot 4H_2O(s) + aq \longrightarrow Ca(NO_3)_2(aq) + 4H_2O(l)$; $\Delta H_2 = +32{,}270$ j.

Subtracting (2) from (1) gives

(3) $Ca(NO_3)_2 \cdot 3H_2O(s) + H_2O(l) \longrightarrow Ca(NO_3)_2 \cdot 4H_2O(s)$; $\Delta H_3 = -16{,}120$ j.

Here the symbol (aq) refers to infinite dilution, and $\Delta H_3$ is the change in heat content for the hydration process.

**Calculation of Heats of Hydration from Vapor Pressure Data.**—Equation (3) is a specific example of the equilibrium involved in the process of hydration. This equilibrium can be expressed by the general form of a chemical equation

(4) $MA \cdot xH_2O(s) + yH_2O(l) \longrightarrow MA \cdot (x + y)H_2O(s)$; $\Delta H = z$ joules.

This heat of hydration can be calculated by resolving the reaction into a three-stage process. *Step 1* consists of the isothermal evaporation of $y$ moles of water to form water vapor at its vapor pressure at, for example, 25°.

(5) $H_2O(l) \longrightarrow H_2O$(g. at 23.8 mm.); $\Delta H = +43{,}890$ j.

*Step 2* consists of the process of expansion of $y$ moles of water vapor, at the vapor pressure of water, to the pressure that exists in equilibrium with the mixture of crystals.

(6) $H_2O$ (g. at 23.8 mm.) $\longrightarrow H_2O$ (g. at 4.5 mm.); $\Delta H = 0$ j.

since $\Delta H = 0$ for the isothermal expansion of a perfect gas. *Step 3* consists of the reaction of the anhydride or the lower hydrate with $y$ moles of water vapor to form the higher hydrate

(7) $Ca(NO_3)_2 \cdot 3H_2O(s) + H_2O$ (g. at 4.5 mm.) $\longrightarrow Ca(NO_3)_2 \cdot 4H_2O(s)$; $\Delta H = -60{,}800$ j.

If it is assumed that the partial molal volume of the $y$ moles of water of hydration in the crystals is negligible compared to its volume in the vapor state and that the vapor behaves as a perfect gas at the low vapor pressures

[5] Lange and Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

TABLE II

INTEGRAL HEATS OF SOLUTION

$Ca(NO_3)_2(s) + aq \longrightarrow Ca(NO_3)_2\ (aq)$ ; $\Delta H = -19{,}250$ j.

$Ca(NO_3)_2 \cdot 2H_2O(s) + aq \longrightarrow Ca(NO_3)_2\ (aq) + 2H_2O(l)$; $\Delta H = +11{,}770$ j.

$Ca(NO_3)_2 \cdot 3H_2O(s) + aq \longrightarrow Ca(NO_3)_2\ (aq) + 3H_2O(l)$; $\Delta H = +16{,}150$ j.

$\alpha Ca(NO_3)_2 \cdot 4H_2O(s) + aq \longrightarrow Ca(NO_3)_2\ (aq) + 4H_2O(l)$; $\Delta H = +32{,}270$ j.

$Sr(NO_3)_2(s) + aq \longrightarrow Sr(NO_3)_2\ (aq)$ ; $\Delta H = +17{,}540$ j.

$Sr(NO_3)_2 \cdot 4H_2O(s) + aq \longrightarrow Sr(NO_3)_2\ (aq) + 4H_2O(l)$; $\Delta H = +51{,}450$ j.

TABLE III

CHANGES IN HEAT CONTENT, AND IN FREE ENERGY, IN JOULES AT 25°

| Reaction | $\Delta H$ Experimental | $\Delta H$ Calculated | $-\Delta F$ Calculated |
|---|---|---|---|
| $Ca(NO_3)_2(s) + 2H_2O(l) \longrightarrow Ca(NO_3)_2 \cdot 2H_2O(s)$ | −31,000 | −30,800 | 11,780 |
| $Ca(NO_3)_2(s) + 4H_2O(l) \longrightarrow Ca(NO_3)_2 \cdot 4H_2O(s)$ | −51,500 | −59,700 | 20,480 |
| $Ca(NO_3)_2 \cdot 2H_2O(s) + H_2O(l) \longrightarrow Ca(NO_3)_2 \cdot 3H_2O(s)$ | − 4,400 | −11,500 | 5,130 |
| $Ca(NO_3)_2 \cdot 2H_2O(s) + 2H_2O(l) \longrightarrow Ca(NO_3)_2 \cdot 4H_2O(s)$ | −20,500 | −17,200 | 8,820 |
| $Ca(NO_3)_2 \cdot 3H_2O(s) + H_2O(l) \longrightarrow Ca(NO_3)_2 \cdot 4H_2O(s)$ | −16,100 | −16,900 | 4,130 |

of the hydrates, the Clapeyron–Clausius equation can be applied to such systems in the form

$$\frac{d \ln p}{d(1/T)} = -\frac{\Delta H}{R} \quad (8)$$

where $-\Delta H$ is the heat of hydration when the anhydride or a lower hydrate unites with water vapor to form a higher hydrate. This permits us to calculate $\Delta H$ for equation (7). The sum of these three steps gives the heat of hydration with liquid water represented in reaction 3 above. These values, calculated from vapor pressure data, are tabulated in Table III, column 3, for comparison with the experimental heats.

**Accuracy of Results.**—The sources of error in calculated and observed heats of solution must be considered. Individual determinations of the heat capacity of the calorimeter were consistent to within 28 joules in a total of 4500 joules. This corresponds to a temperature error of less than 0.004°, the limit of reliability of a mercury-in-glass thermometer graduated in 0.01°.[6]

A mathematical analysis of the data in Table I indicates that the error in measurement of heats of solution varies from 0.3 to 3%. The errors in measuring the heats of solution are considerably larger than the error in determining the heat capacity of the calorimeter. These are caused in large part by difficulty in preparing the hydrates in a pure state. This was particularly true of $Ca(NO_3)_2 \cdot 3H_2O$ and $Ca(NO_3)_2 \cdot 2H_2O$ since they had to be prepared from concentrated, viscous solutions at high temperatures.

Errors in calculating heats of hydration from vapor pressures are: (1) Errors due to vapor pressure measurements. These amount to ±900 joules, corresponding to an error of ±0.05 mm. (2) Uncertainty of at least 0.1% in latent heats of vaporization. This corresponds to from 50 to 200 joules. (3) Errors in the Clapeyron–Clausius equation introduced by assuming water vapor to be a perfect gas. This amounts to from 190 joules to 760 joules. Thus the maximum deviation in the calculated heats of hydration is 4560 joules or, at most, 13.3%.

It is interesting to compare observed values of vapor pressure with those calculated from heats of hydration. Taking $T$ as 25° and $\Delta(1/T)$ as 0.0001, we find at 35°

| Equilibrium | Tetra–tri. | Tetra–di. | Tetra–anhyd. | Tri–di. | Di–anhyd. |
|---|---|---|---|---|---|
| Calcd. vapor pressure, mm. | 9.9 | 8.1 | 6.3 | 5.1 | 4.8 |
| Obs. vapor pressure, mm. | 10.0 | 8.0 | 6.5 | 5.5 | 4.9 |

In general, the concordance is very satisfactory.

**Free Energy of Hydration.**—An expression for the free energy change, $\Delta F$, for the hydration process can be derived by letting the process take place in the three steps already mentioned. For steps 1 and 3

$$-\Delta F = 0 \quad (9)$$

[6] Bureau of Standards Circular No. 8.

Step 2 consists of the isothermal expansion of water vapor. If water vapor behaves as a perfect gas, $\Delta pv = 0$, and

$$-\Delta A = -\Delta F = nRT \ln (p_w/p_s) \quad (10)$$

The sum of these three steps leaves equation (10) as the decrease in free energy of the hydration process. The decrease in free energy is tabulated in Table III, column 4.

**Change in Heat of Hydration and Change in Free Energy with Change in Temperature.**—Since ln $p$ plotted against $1/T$ gives a straight line, step 3 in the hydration process, that is, the heat of hydration with water vapor, remains constant at various temperatures. The change in heat of hydration with liquid water with change in temperature, then, is due to changes in the latent heat of vaporization of water with change in temperature. Heats of hydration and latent heats are tabulated in Table IV for the system

$$Ca(NO_3)_2 \cdot 3H_2O(s) + H_2O(l) \longrightarrow Ca(NO_3)_2 \cdot 4H_2O(s)$$

Values for the decrease in free energy, $-\Delta F$, for the same process, calculated by means of equation (10) at various temperatures, are tabulated in the same table.

TABLE IV

$\Delta H$ AND $-\Delta F$ AT VARIOUS TEMPERATURES

| Temp..... | 20°C. | 25°C. | 30°C. | 35°C. | 40°C. |
|---|---|---|---|---|---|
| Step 1. | +44,102 j. | +43,886 j. | +43,688 j. | +43,481 j. | +43,273 j. |
| Step 3 | −60,800 | −60,800 | −60,800 | −60,800 | −60,800 |
| $\Delta H$ | −16,698 | −16,914 | −17,112 | −17,319 | −17,527 |
| $p_w/p_s$ | 17.5/3.0 | 23.8/4.5 | 31.8/6.8 | 42.2/10.0 | 55.3/14.8 |
| $-\Delta F$ | +4299 | +4129 | +3888 | +3689 | +3432 |

This table shows that there is a small increase in heat of hydration and a small decrease in the decrease in free energy with increasing temperatures for this reaction.

## Summary

Integral heats of solution of the hydrates and the anhydride of calcium nitrate and of strontium nitrate have been measured.

Heats of hydration have been calculated from these heats of solution. The same heats of hydration have been calculated from the latent heat of vaporization of water and the vapor pressure–temperature measurements above both the stable and the metastable eutectic mixtures of crystals.

The change in free energy of hydration has been calculated.

The changes in heat content and in free energies of hydration with change in temperature have been calculated.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# THE INDIRECT VOLUMETRIC DETERMINATION OF SODIUM BASED ON THE REDUCTION AND TITRATION OF THE URANIUM IN MAGNESIUM SODIUM URANYL ACETATE[1]

BY N. HOWELL FURMAN, EARLE R. CALEY AND IRL C. SCHOONOVER[2]

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## Introduction

The advantages of the direct gravimetric determination of sodium as hydrated sodium magnesium uranium triacetate ($Mg(C_2H_3O_2)_2 \cdot NaC_2H_3O_2 \cdot 3UO_2(C_2H_3O)_2 \cdot 6.5H_2O$) have been demonstrated by Caley and Foulk.[3] They have also described a rapid colorimetric method based upon color of the uranium salt; this method is limited to quantities of 5 mg. or less of sodium.

Caley[4] obtained good results in the volumetric estimation of sodium by titration of the uranium in the solution of the triple acetate precipitate with standard sodium phosphate solution. The reduction of the uranium, followed by titration with standard oxidizing agent, should offer even greater advantages because twice as much standard solution of equivalent strength should be used, as in the sodium phosphate procedure.

Subsequent to the completion of the work which is described in this paper, Dobbins and Byrd[5] have described a method for the indirect determination of sodium by titration of the uranium in the sodium–zinc–uranyl acetate precipitate with standard sodium hydroxide; 10 moles of sodium hydroxide are used up per mole of precipitate.

Nau[6] proposed the indirect determination of sodium by reduction of the uranium of the triple acetate precipitate by zinc. Kahane[7] proposed that aluminum or copper be used as a reducing agent. In both cases the reduced solution was poured or filtered away from the excess of metal. The questions of over-reduction and of oxidation of quadrivalent uranium by air in hot solutions were not studied.

In this investigation we have applied the results of a study of the potentiometric determination of uranium that has been made by Furman

[1] Presented at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., September, 1931.

[2] Merck Fellow in Chemistry.

[3] Caley and Foulk, THIS JOURNAL, **51**, 1664 (1929); in this paper the modified reagent suggested by Caley and Sickman, *ibid.*, **52**, 4247 (1930), was used. Applications of the method are described by Caley and Foulk, *J. Am. Water Works Assoc.*, **22**, 970 (1930); Caley, *Ind. Eng. Chem., Analyt. Ed.*, **1**, 191 (1929).

[4] Caley, THIS JOURNAL, **52**, 1349 (1930).

[5] Dobbins and Byrd, *ibid.*, **53**, 3288 (1931).

[6] Nau, *Bull. soc. phar. Bordeaux*, **65**, 67 (1927); *Chem. Abstracts*, **24**, 4236 (1930).

[7] Kahane, *Bull. soc. chim.*, [4] **47**, 382 (1930).

and Schoonover.[8] In this study the presence of chloride was found to be undesirable, but moderate amounts of acetate or of acetic acid did not influence the accuracy of the uranium determination, when standard permanganate or ceric sulfate was used to reoxidize the tri- and quadrivalent uranium which are produced when the uranium solution is passed through the Jones reductor. Ewing and Wilson[9] found that the presence of hydrochloric acid caused the end-point of the process $U^{III} \longrightarrow U^{IV}$ to be so slow as to be impractical; they reported that the presence of acetate caused the end-point of the oxidation $U^{IV} \longrightarrow U^{VI}$ to be erratic. Further tests of the effect of acetate (not detailed here), together with the numerous determinations which are presented in this paper, have convinced us that the acetate which is present in the sodium magnesium uranyl acetate precipitates is without influence upon the accuracy of the uranium titration.

The majority of the determinations here presented were made by determining potentiometrically the two inflections in the titration of the reduced uranium solution. A few determinations were made by the more rapid procedure of removing the trivalent uranium by aeration of the solution. The end of this process is detected potentiometrically; a sudden change of about 0.4 volt occurs (cell: normal calomel electrode, satd. potassium sulfate, uranium solution, Pt). The air is then displaced by a rapid stream of carbon dioxide, and the quadrivalent uranium is titrated at 85–90°.

It was found that the reduced uranium solution could be aerated to oxidize the trivalent uranium, after which a measured excess of standard ceric sulfate was added. Oxidation of the uranium to the hexavalent condition was complete in less than five minutes. The excess of ceric sulfate was determined by back-titration with ferrous sulfate (freshly standardized potentiometrically against ceric solution). This procedure, though indirect, greatly simplifies the volumetric determination of uranium. The application of this simplified method to the determination of sodium was studied.

## Experimental

**Materials and Apparatus.**—The apparatus described by Furman and Schoonover[8] was used. The top of the reductor was provided with a Gooch crucible holder, so that the sodium magnesium uranyl acetate could be dissolved in 2% sulfuric acid and drawn directly from the crucible into the reductor by suction.

The magnesium uranyl acetate reagent was prepared as described by Caley and Sickman.[3] The sodium precipitate was washed with alcohol saturated with the precipitate, and the excess of alcohol was removed by drying. The technique described by Caley and Foulk[3] was followed in the precipitation and gravimetric determinations of sodium, and that of Furman and Schoonover in the volumetric work.

Known sodium solutions were prepared from pure dry sodium chloride and stored in bottles of Pyrex glass.

[8] Furman and Schoonover, THIS JOURNAL, **53**, 2561 (1931).

[9] Ewing and Wilson, *ibid.*, **53**, 2105 (1931).

In the preliminary test analyses known amounts of the sodium chloride solutions were pipetted out, evaporated to 5 cc. or less, and treated with the proper amount of the magnesium uranyl acetate reagent. The amounts of sodium were determined gravimetrically, and then by titration of the solution of the precipitate after reduction of the uranium. In Table I are given the results of a number of determinations made with standard permanganate. The percentages of $UO_2$ in the precipitates are derived from the weights of the precipitates and the volumes of the permanganate used. It is probable that the gravimetric determinations are better values for the amounts of sodium actually present than those calculated (column 1) from the amounts of sodium solution pipetted out.

TABLE I

INDIRECT VOLUMETRIC DETERMINATION OF SODIUM WITH 0.1147 *N* $KMnO_4$

| No. | 1 Na present calcd., g. | 2 Na found grav., g. | 3 Na found vol., g. | 4 $KMnO_4$ used, cc. | 5 Error grav., mg. | 6 Error vol., mg. | 7 $UO_2$ in ppt., % |
|---|---|---|---|---|---|---|---|
| 1 | 0.0200 | 0.02003 | 0.01999 | 45.48 | 0.03 | −0.01 | 53.83 |
| 2 | .0200 | .02002 | .01998 | 45.46 | .02 | − .02 | 53.83 |
| 3 | .0100 | .00996 | .00977[a] | 22.22 | − .04 | − .23 | 52.98[a] |
| 4 | .0100 | .00999 | .00986[a] | 22.42 | − .01 | − .14 | 53.20[a] |
| 5 | .0100 | .00998 | .00983[a] | 22.38 | − .02 | − .17 | 53.16[a] |
| 6 | .0100 | .00999 | .00999 | 22.74 | − .01 | − .01 | 53.92 |
| 7 | .0100 | .00999 | .00999 | 22.74 | − .01 | − .01 | 53.93 |
| 8 | .0100 | .01000 | .00998 | 22.73 | .00 | − .02 | 53.88 |
| 9 | .0100 | .01000 | .01000 | 22.77 | .00 | .00 | 53.69 |
| 10 | .0050 | .00497 | .00499 | 11.37 | − .03 | − .01 | 54.48 |
| 11 | .0050 | .00493 | .00498 | 11.33 | − .07 | − .02 | 54.48 |
| 12 | .0050 | .00495 | .00499 | 11.37 | − .05 | − .01 | 54.42 |
| 13 | .0010 | .00104 | .00102 | 2.34 | .04 | .02 | 54.27 |
| 14 | .0010 | .00100 | .00100 | 2.27 | .00 | .00 | 54.00 |

[a] These three determinations were known to be imperfect because of loss of uranium solution by diffusion into an improperly constructed salt bridge.

A similar series of determinations was made using standard ceric solutions in the titrations. The results are presented in Table II.

TABLE II

INDIRECT VOLUMETRIC DETERMINATION OF SODIUM USING STANDARD CERIC SULFATE

Determinations 2–4 and 6–8 were made with 0.1043 *N* ceric sulfate

| No. | 1 Na present calcd., g. | 2 Na found grav., g. | 3 Na found vol., g. | 4 $Ce(SO_4)_2$ used, cc. | 5 Error grav., mg. | 6 Error vol., mg. | 7 $UO_2$ in ppt., % |
|---|---|---|---|---|---|---|---|
| 1 | 0.0130 | 0.01309 | 0.01302 | 31.43 | 0.09 | 0.02 | 53.56[a] |
| 2 | .0100 | .01000 | .00999 | 24.99 | .00 | − .01 | 53.77 |
| 3 | .0100 | .00999 | .00998 | 24.97 | − .01 | − .02 | 53.84 |
| 4 | .0100 | .00999 | .01000 | 25.02 | − .01 | .00 | 53.97 |
| 5 | .0080 | .00793 | .00793 | 19.16 | − .07 | − .07 | 53.91[a] |
| 6 | .0050 | .00495 | .00498 | 12.46 | − .05 | − .02 | 54.29 |
| 7 | .0050 | .00496 | .00499 | 12.48 | − .04 | − .01 | 54.20 |
| 8 | .0050 | .00495 | .00499 | 12.49 | − .05 | − .01 | 54.40 |

[a] One of us (C.) made the gravimetric determination, and another (F.) the volumetric using 0.1079 *N* ceric sulfate, without information as to the amount of sodium until after the titrations had been made.

**Rapid Titration of Reduced Uranium Solutions.**—From thirty to forty minutes are required for the reduction of the uranium and the potentiometric titration. An atmosphere of carbon dioxide is necessary in the direct potentiometric titration. We have found that the determination of the reduced uranium may be greatly simplified, and the use of carbon dioxide dispensed with.

**Procedure.**—The uranium solution, at room temperature, is passed through a Jones reductor. The reduced solution is stirred for five minutes while a rapid stream of air is being passed through. The end of this process may be determined potentiometrically, although this is not necessary. A measured excess of standard ceric sulfate is added, and the solution is stirred vigorously for five minutes. The excess is then determined by back-titration with standardized ferrous sulfate solution.[10] Some results of this method of determination are given in Table III. In each case 24.75 cc. of 0.2115 *N* $Ce(SO_4)_2$ was used.

TABLE III

DETERMINATION OF URANIUM WITH 0.2115 *N* CERIC SULFATE

| | 1 Uranium present, g. | 2 $FeSO_4$ used, cc. | 3 $Ce(SO_4)_2$ used, cc. | 4 Uranium found, g. | 5 Error, mg. |
|---|---|---|---|---|---|
| 1 | 0.2792 | 37.58 | 11.10 | 0.2795 | +0.3 |
| 2 | .2792 | 37.63 | 11.06 | .2783 | − .7 |
| 3 | .2792 | 37.55 | 11.08 | .2790 | − .2 |
| 4 | .2779 | 37.68 | 11.05 | .2783 | + .4 |
| 5 | .2779 | 37.70 | 11.04 | .2780 | + .1 |
| 6 | .2779 | 37.68 | 11.05 | .2783 | + .4 |

**Application to Sodium Determination.**—The rapid titration method was applied to the determination of sodium in portions of a sodium chloride

TABLE IV

DETERMINATION OF SODIUM BY RAPID INDIRECT METHOD

| Sodium present, g. | $Ce(SO_4)_2$ used by $U^{IV}$ cc. of 0.2080 *N* | Sodium found, g. | Error, mg. |
|---|---|---|---|
| 0.0050 | 6.32 | 0.00504 | 0.04 |
| .0050 | 6.28 | .00501 | .01 |
| .0050 | 6.23 | .00497 | −.03 |
| .0100 | 12.63 | .01007 | .07 |
| .0100 | 12.62 | .01006 | .06 |
| .0200 | 25.16 | .02006 | .06 |
| .0200 | 25.14 | .02004 | .04 |

[10] The potentiometric method was used. In some of the determinations listed in Table IV, it was found that erioglaucine indicator changed color at the potentiometric end-point, and that the presence of uranium did not interfere [see Furman and Wallace, THIS JOURNAL, **52**, 2357 (1930)]. The indicator method was proved to be accurate for this titration by comparative study with the potentiometric method in a number of determinations which will not be described here.

solution of known concentration. The results are presented in Table IV. From 15 to 35 cc. of 0.2080 *N* ceric sulfate was added to the solutions of $U^{IV}$.

**Applications of the Method.**—One of us (S.) analyzed a silicate the composition of which was unknown to him. The samples of the material were treated in a platinum dish with hydrofluoric acid until decomposition was effected, and finally the fluorides were transposed to sulfates with a very small excess of sulfuric acid; most of the latter acid was volatilized. The sodium was then precipitated, and determined both gravimetrically and volumetrically.

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Wt. of sample, g. | 0.3334 | 0.3100 | 0.3210 | 0.3056 |
| Wt. of triple acetate, g. | 0.3995 | 0.3662 | 0.3785 | 0.3610 |
| $Na_2O$, grav., % | 2.46 | 2.43 | 2.42 | 2.43 |
| Cc. stand. soln. | 15.48 | 15.00 | 12.98 | 12.42 |
| $Na_2O$, vol. % | 2.28 | 2.37 | 2.40 | 2.41 |

Determinations 1 and 2 were made with 0.0949 *N* ceric solution, and 3 and 4 with 0.1147 *N* permanganate solution.

The material was a Bureau of Standards feldspar containing 2.38% of $Na_2O$ according to the Bureau. Caley found an average of 2.33% $Na_2O$ by the direct gravimetric triple acetate method after decomposing the sample by the J. Lawrence Smith method.

The sodium present in a sample of crystallized aluminum sulfate was determined by the aeration and direct potentiometric procedures. Found: 0.220, 0.220, 0.226; present 0.231% of sodium.

The rapid procedure (aeration, addition of excess of $Ce(SO_4)_2$ and back-titration) was applied to the determination of sodium in a mixture of pure sodium and potassium chlorides of composition unknown to the operator (S). The ceric sulfate was 0.2080 *N*.

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Wt. of sample, g. | 0.1390 | 0.1410 | 0.1837 | 0.1468 |
| $Ce(SO_4)_2$ used, cc. | 10.38 | 10.37 | 13.84 | 11.14 |
| Sodium found, % | 5.95 | 5.86 | 6.01 | 6.05 |

The material contained 5.90% of sodium (15% NaCl, 85% KCl). These results were considered to be satisfactory, especially in view of the large proportion of potassium in the sample.

**Discussion.**—The results which have been presented prove that permanganate or ceric sulfate solutions standardized against pure sodium oxalate may be used for the indirect estimation of sodium; with good technique the absolute error in the determination of the sodium should be less than 0.1 mg.

The variations in the percentage of $UO_2$ in the precipitate are of considerable interest. For the larger amounts of sodium, the percentage of

$UO_2$ is distributed within a small range of the value 53.79% which is calculated on the basis that the triple salt contains 6.5 molecules of water of crystallization when formed by Caley and Foulk's procedure. When small amounts of sodium are precipitated, there is apparently a change in the composition of the precipitate during washing and the percentage of uranyl is high. Caley attributes this change to partial solution of magnesium acetate during the washing. The sodium–uranium ratio appears to be practically constant for amounts of sodium as low as 1 mg. The indirect volumetric method appears to offer advantages over the gravimetric for the determination of amounts of sodium ranging from 1 to 10 mg.

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## Summary

The sodium present in triple sodium magnesium uranyl acetate may be determined indirectly by reduction and titration of the uranium. The method appears to offer advantages over other methods in respect to accuracy when quantities of sodium below 10 mg. are to be determined.

The volumetric method gives significant evidence of the constancy of composition of the precipitates obtained from amounts of sodium ranging from 0.01 to 0.02 g. Although the percentage of $UO_2$ is somewhat higher than the theoretical value in precipitates of small weight, the ratio of sodium to uranium in these precipitates appears to be constant in the range studied.

A technique for the rapid indirect determination of uranium or of sodium has been developed.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

# THE DISSOCIATION CONSTANT OF ACETIC ACID FROM 0 TO 35° CENTIGRADE[1]

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Recently, Harned and Owen[1a] have shown that it is possible to determine the dissociation constants of weak acids from cells without liquid junctions of the type

$$H_2/HAc(M),\ NaCl(m)/AgCl/Ag$$

From the results of Harned and Robinson,[2] they computed the dissociation constant of acetic acid, and from their own data that of formic acid, both at 25°. The value obtained for the dissociation constant of acetic acid was $1.75 \times 10^{-5}$, which was considerably lower than the usually accepted value, but agrees with the value of $1.747 \times 10^{-5}$ computed from conductance measurements as recently reported by MacInnes and Shedlovsky.[3] Since our value was determined from measurements which were not made for this purpose, we have redetermined this constant by a somewhat different method by employing the cell

$$H_2/HAc(m_1),\ NaAc(m_2),\ NaCl(m_3)/AgCl/Ag$$

which is seen to contain an acetic acid–sodium acetate buffer mixture. To extend our knowledge of this subject, the dissociation constant has been evaluated at 0, 5, 10, 15, 20, 25, 30 and 35°.

## Discussion of the Method

The electromotive force of the cell in question is given by the well-known equation

$$E = E_0 - \frac{RT}{F} \ln \gamma_H \gamma_{Cl}\, m_H m_{Cl} \qquad (1)$$

The thermodynamic equation for the dissociation of acetic acid is

$$K = \frac{\gamma_H \gamma_{Ac}}{\gamma_{HAc}} \frac{m_H m_{Ac}}{m_{HAc}} \qquad (2)$$

$K$ is the dissociation constant of the acid, the "$\gamma$'s" and "$m$'s" represent the activity coefficients and molal concentrations of the ionic species denoted by subscripts, and $E_0$ is the normal electrode potential of the cell

$$H_2/HCl(m)/AgCl/Ag$$

Upon eliminating $m_H$ from equations (1) and (2), and rearranging terms, we obtain

[1] The present communication contains material which represents part of a Thesis to be presented by Russell W. Ehlers to the Graduate School of Yale University in partial fulfilment of the degree of Doctor of Philosophy, June, 1932.

[1a] Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

[2] Harned and Robinson, *ibid*, **50**, 3157 (1928).

[3] MacInnes and Shedlovsky *ibid*., **53**, 2419 (1931).

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{HAc} m_{Cl}}{m_{Ac}} = - \frac{RT}{F} \ln \frac{\gamma_H \gamma_{Cl} \gamma_{HAc}}{\gamma_H \gamma_{Ac}} - \frac{RT}{F} \ln K \qquad (3)$$

This equation is extraordinarily easy to use if the values of $E_0$ are known at the desired temperatures. The first member on the right contains the logarithm of the ratio of two ionic activity coefficient products. This ratio equals unity at infinite dilution and varies little from unity at low ionic strengths. This is also true for $\gamma_{HAc}$. Further, the logarithm of such a quantity as this ratio is known to vary linearly with the ionic strength. Therefore, if the quantity on the left side of this equation be plotted against the ionic strength, $\mu$, a curve which is very nearly straight should be obtained. The intercept at $\mu$ equals zero will be $-(RT/F) \ln K$, from which $K$ may easily be computed.

A second method, and the one which we have employed, is as follows: Let the right-hand side of equation (3) equal $-(RT/F) \ln K'$: If $K'$ be plotted against $\mu$, its intercept at zero $\mu$ is $K$, since the activity coefficients become unity at infinite dilution. Indeed, in the present case, this method is as good as the first, since the plot of $K'$ against $\mu$ has no greater curvature than the plot of log $K'$ against $\mu$ at the lower concentrations.

The evaluation of the left-hand side of equation (3) is readily made. $m_{Cl}$ is known, $m_{HAc}$ equals $m_1 - m_H$, and $m_{Ac}$ equals $m_2 + m_H$. If an approximate value of $K$ be used, then $m_H$ may be computed and $m_{HAc}$ and $m_{Ac}$ evaluated.[4] Thus, since all the terms on the left are capable of being known, $K'$ and subsequently $K$ may readily be evaluated.

## Preparation of Solutions and Experimental Procedure

(1) **Materials.**—Sodium acetate was purified by three recrystallizations of a high grade analyzed salt from conductivity water. The solutions were never boiled, so that loss of acetic acid by evaporation from the hydrolyzed salt solution was avoided. The crystals were dried by suction.

Sodium chloride was recrystallized twice from conductivity water.

Acetic acid was distilled four times, the first three from a 2% (2 g. per 100 g. of acetic acid) solution of chromic anhydride, in an all-glass still through an efficient fractionating column. The first and last quarters were always discarded.

(2) **Solutions.**—Water of specific conductance of $10^{-6}$ was used in the preparation of all solutions. Stock solutions of sodium acetate, sodium chloride, and acetic acid approximately 1 $M$ were prepared and these were standardized as follows.

(a) The sodium chloride and hydrochloric acid solutions were analyzed by determining the chloride content by precipitation of silver chloride. Their molalities were known to within 1 part in 3000, or 0.03%.

(b) The sodium acetate solution was analyzed by evaporation of a 5-g. sample with sulfuric acid. This was carried out very slowly in a muffle furnace where the heat was distributed with sufficient uniformity so that any spattering was avoided. When

[4] As far as this correction is concerned, we have found that a change in $K$ from $1.65 \times 10^{-5}$ to $1.75 \times 10^{-5}$ causes a change in $K'$ of only one in the third decimal place. Since $K$ may readily be estimated within their much narrower limits than the above, any error due to this correction is negligible.

the fumes of sulfur trioxide appeared, air saturated with ammonia was passed over, and the evaporation continued to the final stage. The quantity of sodium sulfate weighed was approximately 0.5 g. The analyses checked to within 0.05%.

(c) Acetic acid was standardized by titration against a carbonate-free sodium hydroxide solution whose strength was determined by titration against a very carefully analyzed hydrochloric acid solution. Weight burets were employed and vacuum corrections made when necessary. The values of the molalities represent the average of numerous determinations which agreed within 0.1% of the total acetic acid. The molality of the acetic acid was therefore known to at least 1 part in 1000, or 0.1%.

**(3) Experimental Procedure.**—The cells were of the customary kind for this purpose, and were arranged so that they could be filled in vacuum. The hydrogen electrodes were of platinum foil (1.5 × 3 cm.) and a deposit of platinum black formed by 0.5 ampere per electrode for three minutes was found very satisfactory. The silver–silver chloride electrodes were of the type (2) described by Harned.[5]

The solutions were prepared by weighing portions of the standardized solutions in weighed flasks. Appropriate amounts of water were added and the solutions boiled under reduced pressure. Hydrogen was then admitted into the flasks above the solutions. The loss in weight by boiling was assumed to be water. The cells were filled by employing vacuum technique.

For the preliminary measurements, the same solution and electrodes were used throughout the entire temperature range of from 0 to 35°. Sometimes thirty hours were necessary for these measurements and frequently cells containing solutions of the same concentration would barely agree within 0.1 mv., especially if the initial temperature was 0°. For this reason, the final results recorded were made in two series. The first was from 0 to 20° and the second from 15 to 35°. Duplicate cells checked within a few hundredths of a millivolt. All reported results of the electromotive forces of the cells containing the acetic acid are averages of six cells.

Ice was used to cool the thermostat to a temperature of 0.1 to 0.2°. The temperature was not changed until the readings were constant over a period of forty-five minutes. Two thermometers calibrated against a standard thermometer were placed at the ends of the thermostat. No variation in temperature was noticeable and the control was within ±0.01°. All electromotive forces are calculated for 1 atm. pressure of hydrogen.

**Electromotive Forces of the Cells: $H_2/HCl(m)/AgCl/Ag$ and the Evaluation of $E_0$.**—Table I contains the measurements of the cells containing the hydrochloric acid. The following procedure was adopted to compute $E_0$. The equation for the cells may be written

$$E + 2k \log m = E_0 - 2k \log \gamma \qquad (4)$$

where $k$ equals $2.3026\ RT/NF$. The left side of this equation was first plotted on a large scale against $m^{1/2}$. The results at round concentrations read from this very sensitive family of graphs are given in Table II. The evaluation of $E_0$ at each temperature was made by the method suggested by Hitchcock.[6] In dilute solutions, log $\gamma$ varies according to the law

$$\log \gamma = -0.5\, m^{1/2} + bm \qquad (5)$$

Combining with equation (4) and rearranging, we obtain

$$E + 2k \log m - km^{1/2} = E_0 - 2kbm \qquad (6)$$

[5] Harned, THIS JOURNAL, **51**, 416 (1929).

[6] Hitchcock, *ibid.*, **50**, 2076 (1928).

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS: $H_2/HCl(m)/AgCl/Ag$

| $m$ | $E_0'$ | $E_5$ | $E_{10}$ | $E_{15}$ | $E_{20}$ | $m$ | $E_{15}$ | $E_{20}$ | $E_{25}$ | $E_{30}$ | $E_{35}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.003215 | 0.50933 | 0.51196 | 0.51436 | 0.51662 | 0.51864 | 0.003215 | | | 0.52053 | 0.52224 | 0.52389 |
| .003661 | .50334 | .50578 | .50800 | .51008 | .51200 | .003564 | 0.51150 | 0.51349 | .51527 | .51693 | .51846 |
| .005314 | .48644 | .48860 | .49054 | .49232 | .49395 | .004488 | .50051 | .50223 | .50384 | .50533 | .50665 |
| .005763 | .48275 | .48484 | .48679 | .48848 | .49003 | .004776 | | | .50084 | .50230 | .50358 |
| .007771 | .46912 | .47091 | .47258 | .47402 | .47530 | .005619 | .48957 | .49110 | .49257 | .49388 | .49504 |
| .008636 | .46435 | .46610 | .46771 | .46905 | .47024 | .006239 | .48461 | .48614 | .48747 | .48869 | .48975 |
| .008715 | .46401 | .46575 | .46727 | .46863 | .46987 | .007311 | .47688 | .47826 | .47948 | .48052 | .48144 |
| .011095 | .45314 | .45468 | .45601 | .45721 | .45823 | .008514 | | | | | |
| .013049 | .44586 | .44725 | .44843 | .44947 | .45039 | .008636 | | | .47135 | .47226 | .47304 |
| .013407 | .44466 | .44596 | .44719 | .44811 | .44899 | .009138 | .46635 | .46757 | .46860 | .46949 | .47024 |
| .013981 | .44273 | .44411 | .44522 | .44620 | .44704 | .009436 | | | .46711 | .46795 | .46868 |
| .016457 | .43544 | .43667 | .43766 | .43850 | .43921 | .011195 | .45672 | .45775 | .45861 | .45934 | .45991 |
| .018369 | .43055 | .43170 | .43260 | .43335 | .43394 | .013500 | .44776 | .44868 | .44938 | .44998 | .45038 |
| .021028 | .42425 | .42526 | .42607 | .42676 | .42726 | .013407 | | | .44974 | | |
| .025630 | .41557 | .41643 | .41718 | .41766 | .41801 | .01473 | .44361 | .44444 | .44512 | .44565 | .44596 |
| .034920 | .40181 | .40240 | .40282 | .40308 | .40318 | .01710 | .43658 | .43725 | .43783 | .43822 | .43844 |
| .041245 | .39426 | .39470 | .39502 | .39515 | .39513 | .02305 | .42253 | .42294 | .42329 | .42346 | .42345 |
| .04935 | .38640 | .38666 | .38685 | .38685 | .38665 | .02563 | | | .41824 | .41830 | .41821 |
| .05391 | .38255 | .38284 | .38299 | .38289 | .38258 | .04749 | .38872 | .38861 | .38834 | .38792 | .38740 |
| .06393 | .37501 | .37508 | .37505 | .37485 | .37443 | .05391 | | | .38222 | .38713 | .38108 |
| .07273 | .36917 | .36921 | .36904 | .36872 | .36823 | .06268 | .37577 | .37545 | .37499 | .37435 | .37362 |
| .08631 | .36167 | .36157 | .36130 | .36085 | .36022 | .09751 | | | .36363 | .35265 | .35158 |
| .09751 | .35610 | .35597 | .35568 | .35511 | .35438 | .12381 | | | .34199 | .34086 | .33963 |
| .12354 | .34567 | .34530 | .34478 | .34402 | .34311 | .005314 | .34383 | .34297 | .49145 | .49275 | .49385 |
| .009436 | .46050 | .46210 | .46359 | .46492 | .46609 | | | | | | |
| .004776 | .49142 | .49360 | .49564 | .49754 | .49930 | | | | | | |

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS: $H_2/HCl(m)/AgCl/Ag$ AT ROUND CONCENTRATIONS

| $m$ | $E_0'$ | $E_5$ | $E_{10}$ | $E_{15}$ | $E_{20}$ | $E_{25}$ | $E_{30}$ | $E_{35}$ |
|---|---|---|---|---|---|---|---|---|
| 0.005 | 0.48916 | 0.49138 | 0.49338 | 0.49521 | 0.44690 | 0.49844 | 0.49983 | 0.50109 |
| .006 | .48089 | .48295 | .48480 | .48647 | .48800 | .48940 | .49065 | .49176 |
| .007 | .47390 | .47584 | .47756 | .47910 | .48050 | .48178 | .48289 | .48389 |
| .008 | .46785 | .46968 | .47128 | .47270 | .47399 | .47518 | .47617 | .47704 |
| .009 | .46254 | .46426 | .46576 | .46708 | .46828 | .46937 | .47026 | .47103 |
| .010 | .45780 | .45943 | .46084 | .46207 | .46319 | .46419 | .46499 | .46565 |
| .02 | .42669 | .42776 | .42862 | .42925 | .42978 | .43022 | .43049 | .43058 |
| .03 | .40859 | .40931 | .40993 | .41021 | .41041 | .41056 | .41050 | .41028 |
| .04 | .39577 | .39624 | .39668 | .39673 | .39673 | .39666 | .39638 | .39595 |
| .05 | .38586 | .38616 | .38641 | .38631 | .38614 | .38589 | .38543 | .38484 |
| .06 | .37777 | .37793 | .37802 | .37780 | .37749 | .37709 | .37648 | .37578 |
| .07 | .37093 | .37098 | .37092 | .37061 | .37017 | .36965 | .36890 | .36808 |
| .08 | .36497 | .36495 | .36479 | .36438 | .36382 | .36320 | .36285 | .36143 |
| .09 | .35976 | .35963 | .35937 | .35888 | .35823 | .35751 | .35658 | .35556 |
| .1 | .35507 | .35487 | .33451 | .35394 | .35321 | .35240 | .35140 | .35031 |
| $E_0$ | .23627 | .23386 | .23126 | .22847 | .22550 | .22239 | .21918 | .21591 |

The left side of equation (6) was plotted against $m$. The graphs have only a very slight curvature and may easily be extrapolated to zero $m$. The ordinate reading gives $E_0$. The values thus obtained at the eight temperatures are given in the bottom row of Table II. The same procedure was adopted at 25° using 0.5065 instead of 0.5 for the universal constant of the Debye and Hückel theory. This was found to make no appreciable difference in the value of $E_0$ obtained since the slope, $2\,kb$, varied simultaneously. From these results and by this method we believe that $E_0$ has been evaluated within ±0.02 mv. Perhaps a different cell technique would give somewhat different values, but since we have employed the same procedure for the cells containing the acetic acid as for the cells under consideration, such a discrepancy would make no error in our final values of the dissociation constant. The value of 0.22239 at 25° agrees very well with that of Roberts[7] who obtained 0.22240 from his electromotive force measurements.

**Measurements of the Cells $H_2/HAc(m_1)$, $NaAc(m_2)$, $NaCl(m_3)/AgCl/Ag$ and the Evaluation of the Dissociation Constant of Acetic Acid.**—In Table III, measurements are given of the cells containing the acetic acid–sodium acetate buffer solutions and sodium chloride. From these results and the values obtained for $E_0$, the values of $K'$ computed by equation (3) are given in the second part of Table III at the ionic strengths designated. In Fig. 1 these values are plotted against the ionic strength. The plots have a definite curvature, but straighten out at the lower concentrations so that the extrapolation may be readily and accurately made. The

[7] Roberts, THIS JOURNAL, **52**, 3877 (1930).

TABLE III

ELECTROMOTIVE FORCES OF THE CELLS: $H_2/HAc(m_1)$, $NaAc(m_2)$, $NaCl(m_3)/AgCl/Ag$

| $m_1$ | $m_2$ | $m_3$ | $E_0'$ | $E_5$ | $E_{10}$ | $E_{15}$ | $E_{20}$ | $E_{25}$ | $E_{30}$ | $E_{35}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.004779 | 0.004599 | 0.004896 | 0.61995 | 0.62392 | 0.62789 | 0.63183 | 0.63580 | 0.63959 | 0.64335 | 0.64722 |
| .012035 | .011582 | .012426 | .59826 | .60183 | .60538 | .60890 | .61241 | .61583 | .61922 | .62264 |
| .021006 | .020216 | .021516 | .58528 | .58855 | .59186 | .59508 | .59840 | .60154 | .60470 | .60792 |
| .04922 | .04737 | .05042 | .56545 | .56833 | .57128 | .57413 | .57699 | .57977 | .58257 | .58529 |
| .08101 | .07796 | .08297 | .55388 | .55667 | .55928 | .56189 | .56456 | .56712 | .56964 | .57213 |
| .09056 | .08716 | .09276 | .55128 | .55397 | .55661 | .55912 | .56171 | .56423 | .56672 | .56917 |

VALUES OF $K'$ AND EXTRAPOLATED VALUES OF THE DISSOCIATION CONSTANT, $K$

| | $K' \times 10^5$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\mu = m_2 + m_3 + m_H$ | $t = 0°$ | 5° | 10° | 15° | 20° | 25° | 30° | 35° |
| 0.00951 | 1.647 | 1.693 | 1.724 | 1.743 | 1.748 | 1.752 | 1.756 | 1.747 |
| .02403 | 1.637 | 1.683 | 1.714 | 1.736 | 1.744 | 1.747 | 1.749 | 1.743 |
| .04175 | 1.627 | 1.675 | 1.707 | 1.733 | 1.738 | 1.743 | 1.745 | 1.736 |
| .09781 | 1.610 | 1.660 | 1.692 | 1.718 | 1.728 | 1.734 | 1.736 | 1.735 |
| .16095 | 1.600 | 1.641 | 1.681 | 1.708 | 1.718 | 1.724 | 1.730 | 1.731 |
| .17994 | 1.598 | 1.643 | 1.678 | 1.709 | 1.720 | 1.726 | 1.731 | 1.731 |
| $K \times 10^5$ | 1.653 | 1.699 | 1.727 | 1.743 | 1.751 | 1.754 | 1.755 | 1.750 |

values of $K$ thus determined at zero $\mu$ are given in the last row of the second part of Table III. The results are of a very high order of accuracy since nearly all points lie within two in the third decimal place from the curves. The maximum deviation which occurs at $0.1\mu$ of the 5° series lies seven in the third decimal place from the curve. This corresponds to an inconsistency of less than 0.1 mv. Since at the lower concentrations the 35° graph lies very near that at 20°, it has been shown on a separate part of the figure. As previously mentioned, the maximum estimated error in analysis occurs with the acetic acid solutions and amounts to $\pm 0.05\%$. This causes an error in $K$ of $\pm 0.001$.

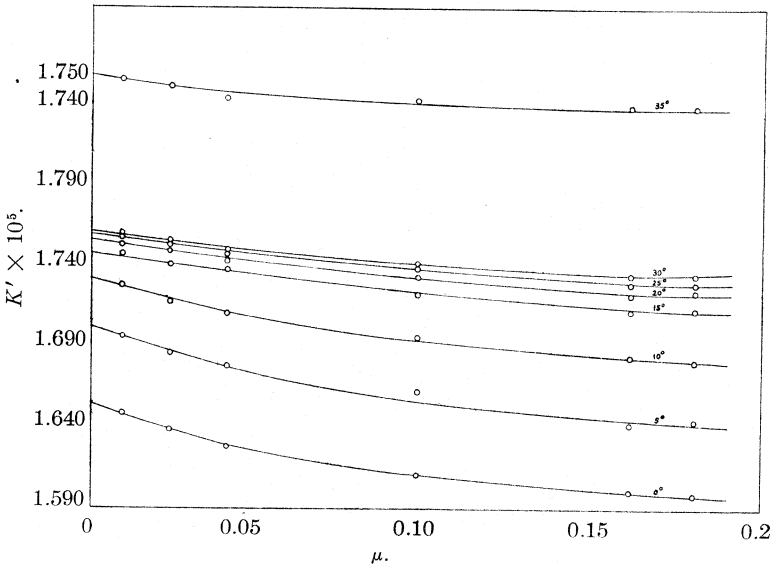


Fig. 1.—Plots of $K'$ against $\mu$ employed in the determination of the dissociation constants.

In Fig. 2 the values of $K$ are plotted against the temperature. The results are very consistent since all points fall on the smooth curve to within one or two in the third decimal place. Further, a maximum is apparent at 30°.

The result we obtain at 25° is $1.754 \times 10^{-5}$, which agrees with the value of $1.75 \times 10^{-5}$ obtained from somewhat different electromotive force measurements by Harned and Owen. Harned and Murphy[8] found that $K$ varied very little between 20 and 30°, and assumed the value of $1.75 \times 10^{-5}$. Our results show a slight variation of four in the third decimal place through this temperature range. The result obtained by the electromotive force methods agrees very well with that of MacInnes and Shed-

[8] Harned and Murphy, THIS JOURNAL, **53**, 8 (1931).

lovsky, who obtained $1.747 \times 10^{-5}$ by very careful conductance measurements. As a result of this agreement, we can say with certainty that $K$ at 25° is known to the second decimal place and is $1.75 \times 10^{-5}$. Further, we have every reason to believe that the results at the other temperatures are as accurate as those at 25°.

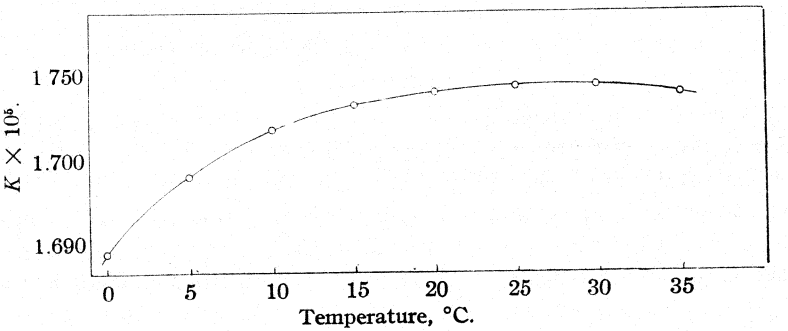


Fig. 2.—The dissociation constant of acetic acid as a function of the temperature.

## Summary

1. Measurements of the cells

$$H_2/HCl(m)/AgCl/Ag$$

at low concentrations of hydrochloric acid have been made at five-degree intervals through a temperature range of 0 to 35°. From these, values of $E_0$ of equation (1) have been evaluated at all temperatures in question.

2. Measurements of the cells

$$H_2/HAc(m_1), NaAc(m_2), NaCl(m_3)/AgCl/Ag$$

have been made at the same temperatures. From these measurements, the dissociation constant of acetic acid has been computed at 0, 5, 10, 15, 20, 25, 30 and 35°. The value of $1.754 \times 10^{-5}$ at 25° agrees well with $1.75 \times 10^{-5}$ obtained by Harned and Owen, and also compares favorably with $1.747 \times 10^{-5}$ obtained by MacInnes and Shedlovsky from conductance measurements.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF NORTHWESTERN UNIVERSITY]

# A STUDY OF THE HEAT CAPACITY AND RELATED THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF LITHIUM CHLORIDE, HYDROCHLORIC ACID AND POTASSIUM HYDROXIDE AT 25°[1]

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## Introduction

This work is a continuation of that begun several years ago by the senior author,[2] with the hope of throwing more light upon the nature of aqueous solutions of electrolytes, through careful determination of their heat capacities and comparison with modern theories of such solutions. The original apparatus was constructed in the Gates Chemical Laboratory of the California Institute of Technology, where the senior author was a National Research Fellow. Professor Arthur A. Noyes very kindly presented it to him to carry on the work begun there. It was then set up in the Wolcott Gibbs Memorial Laboratory, where the senior author was assistant to the late Professor Theodore W. Richards. A few changes and improvements were there made but the press of other work did not permit any additional measurements at that time. Further improvements in the apparatus will be discussed after the brief summary of the method given below.

It is a modification of the Joule–Pfaundler *twin calorimeter* method—a thermal balance. Two almost identical closed calorimeters of slightly over 250 ml. capacity are placed side by side in a *submarine* jacket surrounded by a water-bath. Each is well stirred and supplied with a quantitative heating coil of about 9.5 ohms resistance. The two coils are connected in series so that the same current flows through each and hence the same *relative* amount of heat is always liberated in each. The two calorimeters are brought to nearly the same initial temperature and then heated one degree. The temperature of the water-bath is raised simultaneously, making the process adiabatic. The small difference in temperature between the calorimeters before and after an experiment is measured by means of a multiple thermel connected directly to a sensitive galvanometer. The procedure is like weighing by substitution. In the *working* calorimeter weights, first of water and then of solution, are balanced against a fixed *tare* heat capacity in the second calorimeter. Thus thermally equivalent weights of water and of solution are determined directly and the *specific heat* is obtained by dividing the former by the latter.[3]

[1] Paper presented before the Buffalo meeting of the American Chemical Society, August 31, to September 3, 1931.

[2] Gucker, THIS JOURNAL, 50, 1005 (1928).

[3] For a full description of the apparatus and experimental technique the reader is referred to the original article.[2] A somewhat similar apparatus and references to the

## Apparatus

Three important changes deserve mention. The first was the substitution of spun gold linings for the original gold plating on the calorimeters, in order surely to protect them from any action of the solutions. The second was the use of a 25-ohm four-lead potential type platinum resistance thermometer and Mueller type Wheatstone bridge to measure the temperature of the water-bath before and after the experiment. This excellent apparatus, made by Leeds and Northrup and standardized by the Bureau of Standards, fixed the experimental temperature to 0.01° and is much more sensitive and convenient than the mercury thermometer used for the preliminary work. The third was an improvement in the quantitative heating coils which has further reduced their thermal lag and heat capacity. Each of these simple and satisfactory heaters, illustrated in Fig. 1, was made as follows. Slightly over 1 meter of thin gold tubing 1 mm. in outside diameter was bent into a loop and the two ends pushed through small holes in a threaded brass plug, *A*, protected with a spun gold covering, *B*. The tubing was fastened in place with a minimum amount of hard (silver) solder. A 95-cm. length of No. 30 B. and S. gage "salamander"[4] coated "advance" (constantan) wire was then measured off for the resistance. The insulation was carefully pushed back from each end of the wire, which was filed at an angle of about 60°. A small brass bar served as a jig for this operation. A very small hole, through which the wire would just slip, was bored in one end, which was then ground off at the desired angle as shown. Two pieces of "salamander" coated copper wire of the same size which served as leads were filed in the same manner. The end of each of the wires was carefully tinned and they were joined together with soft solder, using a small iron. The joints were not

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history of the method were described in an article by Richards and Gucker, THIS JOURNAL, **47**, 1876 (1925). The method has also been used recently with great success by Randall and Ramage, *ibid.*, **49**, 93 (1927), and especially by Randall and Rossini, *ibid.*, **51**, 323 (1929).

In the present method the weight of solution is adjusted until the rise of temperature in the two calorimeters is the same (±0.0006°). Temperature measurements are then made under adiabatic conditions with high precision and great simplicity. Randall and his co-workers do not try to balance the temperature rise exactly, but determine the difference in temperature in the two calorimeters, which amounts to 0.01° in many cases. This requires the use of a special potentiometer with the thermel. Lamb and Fairhall (Thesis, Harvard University, 1918) used Richards' thermochemical heating in each calorimeter. This heating could be varied to make the temperature difference practically zero. Apparently no one has tried to *vary the electrical energy input* in one of the calorimeters, although then the rise in temperature could be balanced *without changing the weight of solution*. It does not seem practical to make one of the heaters variable in small known steps, still connecting the two in series so as to have the same current through each. However, it should be a simple matter to connect the two similar heaters in *parallel* and to vary the energy input into one by means of an *external* variable resistance in series with it. The current and voltage drop across the heater will *both* vary with this external resistance and the energy with the *square* of the total resistances. This will cause no serious difficulty in the experiments or calculations and will be tried at an early date in this Laboratory. It should be especially helpful in making measurements over a wide temperature range where, with our present method, any large change in the specific heat would require a different weight of solution.

[4] The trade name for an excellent asbestos coating which can be applied to small wires by the York Insulated Wire Works of the General Electric Company, Bridgeport, Conn.

appreciably larger than the original wire (0.2 mm.). The insulation was carefully pushed back into place so that it completely covered the soldered joint. It was protected against subsequent dislocation by a piece of silk insulation wound over the joint and extending 15 mm. on either side.

A piece of small bare copper wire was now threaded through the gold tubing. One end of the copper lead wire was soldered to it, and the resistance wire was gently pulled inside the gold tubing. The somewhat sticky surface of the "salamander" coating was lubricated with talc, preventing any undue strain on the soldered joints. When in place, the ends of the resistance wire were at *C*, 3 cm. below the ends of the gold tubing. Thus no appreciable amount of the heat generated in the coil escaped from the calorimeter. The tubing was now bent into a loose bifilar coil about 3 cm. in diameter and 6 cm. long, mounted on the calorimeter lid as shown (Fig. 1). A rubber gasket *G* ensured an air-tight joint between the gold casing of the plug *B* and the gold lining *F* of the lid. The No. 30 copper wires[5] were cut off 5 mm. above the lid of the calorimeter and soldered to No. 20 copper leads *L*, *L* of uniform length (6.5 cm.).[6]

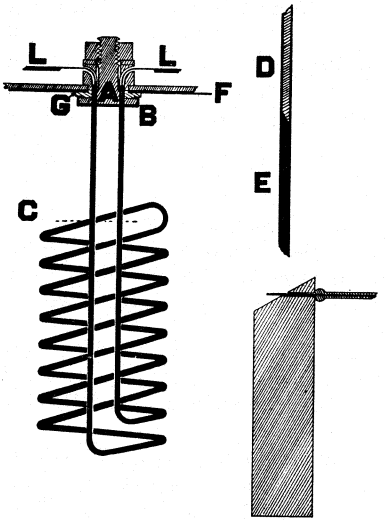


Fig. 1.—Left, heating coil; right top, detail of joint; right bottom, jig for filing fine wires.

The resistance of the two coils differed by only about 0.03% and there was no indication that the ratio of the two resistances was appreciably or permanently changed during the course of the experiments (a year in all).

A three-stage propeller stirrer occupied the space inside the heater and, run at 216 r. p. m., provided an efficient heat dissipation. A higher stirring rate (270 r. p. m.) gave no more rapid thermal equilibrium but caused a 60% increase in the heat of stirring, which was found to increase approximately as the cube of the stirring speed.

The 18-junction thermel originally used to measure the difference in temperature between the calorimeters was replaced by a new 12-junction one, made in two opposable halves. Each junction was insulated from the metal case by means of a small glass capillary tube, which proved to be more satisfactory than the cellulose acetate varnish originally used. The thermel, connected directly as before to a Leeds and Northrup HS galvanometer by means of a simple reversing switch, gave a deflection of 1 mm. on the scale for a difference in temperature of 0.00008°.

## Materials and Solutions

The substances were all prepared, and the solutions made up, analyzed and handled with the care necessary to take full advantage of the calorimetric precision. Fortunately

[5] The "salamander" coating is omitted from the drawing to avoid confusion.

[6] This construction is similar to that used by Randall and Rossini, THIS JOURNAL, **51**, 326 (1929). Decreasing the lead resistance reduces the heat liberated in the leads to 0.04% of that liberated in the calorimeter. Appreciable error due to increased heat conduction is prevented by the careful adiabatic control and the compensation of the twin calorimeters.

extreme care in purification and analysis is not required, since the effect of impurities and the change of specific heat with concentration are both small. Water from the laboratory still, distributed through block tin pipes and containing no known impurity except dissolved air, was used throughout the work. It was freshly boiled (to drive out this air) before use in the calorimeters or in making up solutions.

The best commercial grade of lithium chloride was dissolved in hot water, filtered and twice recrystallized with centrifugal drainage. Probably the most persistent impurity is sodium, for small traces of which a test is very difficult. The method of analysis recommended by Noyes and Bray[7] gave no test for sodium or potassium in a quantity of solution containing 200 mg. of $Li^+$. A comparison test showed that 0.5 mg. of either constituent could easily be detected. The solution therefore contained less than 0.07 mole per cent. of $Na^+$ and 0.05% of $K^+$. Assuming that the change of specific heat is proportional to the mole per cent., the corresponding error in the specific heat of the *two molal* solution is less than 0.004%. The solutions, made up and stored in glass-stoppered Pyrex flasks, were analyzed by means of silver chloride residues.

The hydrochloric acid was made by diluting the best commercial acid to the concentration of the constant boiling mixture. This was slowly distilled from a hard glass flask with constricted neck (like the Richards water still) to which was fitted a Pyrex condenser tube. The middle third of the distillate was collected in a Pyrex or Jena hard glass flask and diluted to the required concentration. Most of the solutions were analyzed by silver chloride residue, although some of the most concentrated ones were titrated against sodium carbonate, made by heating the recrystallized bicarbonate to constant weight in a platinum dish. Titrations were made with weight burets, using methyl orange as an indicator.

The potassium hydroxide was carefully purified by a modification of the method described by Knobel.[8] Two round-bottomed Pyrex flasks, of one and two liter capacity, respectively, were joined by a 15-mm. U-shaped tube, one end of which was sealed to the bottom of each. The inside of flasks and tube was heavily coated with paraffin. Enough purified mercury was put into the apparatus to fill the U-tube and the bottom of each flask. The device was mounted on a rocking table, by which the mercury could be made to flow slowly from one flask to the other. A saturated solution of purest obtainable potassium hydroxide was put into the smaller flask, whence it was slowly electrolyzed into the mercury, which served as cathode. When the resulting amalgam was rocked under the freshly boiled water in the second flask, it reacted to make a very pure solution. A piece of platinized platinum connected to the mercury allowed easy evolution of hydrogen. Once started, the operation was slow but easily controlled and very satisfactory. Using a current of 0.15 ampere, a 2.5 m. solution of potassium hydroxide was produced in two weeks. A higher current gives a more concentrated, viscous amalgam which will not flow properly. The solution was siphoned out of the flask, diluted as desired with freshly boiled water and stored in paraffin-lined bottles, fitted with appropriate siphon tubes and with gas-washing bottles containing some of the solution, to remove carbon dioxide from the entering air. Each concentration of alkali was standardized against a suitable concentration of the hydrochloric acid described above, using weight burets and methyl red as indicator. Inter-comparisons of the different acid and alkali solutions were made to check the concentration of each. The potassium hydroxide solution showed no trace of silica, only 0.01 to 0.02% carbonate and about 0.74 mole per cent. of sodium. This would cause a small error in the most concentrated solutions (0.041% at 2.6 m.) for which due correction was made.

[7] Noyes and Bray, "Qualitative Analysis for the Rarer Elements," The Macmillan Company, New York, 1927. pp. 254 *et seq.*

[8] Knobel, THIS JOURNAL, 45, 70 (1923).

## Experimental Technique

The only change made here was to reduce the temperature interval from 2 to 1°. This made no apparent decrease in the accuracy of the method, partly because the experimental time was reduced and partly because the correction necessary for the slight difference in temperature trend in the two calorimeters was made in a more precise manner. The galvanometer deflection was plotted at one-minute intervals for five minutes before the experiment (which was not started until the trend was uniform) and afterward, until a uniform trend was again obtained for the same length of time.[9] By drawing straight lines through these two *series of points* and extrapolating to the middle of the heating time, the corrected galvanometer change was found more accurately than if only four points had been used.[10] The plot of a typical experiment is given in Fig. 2. As

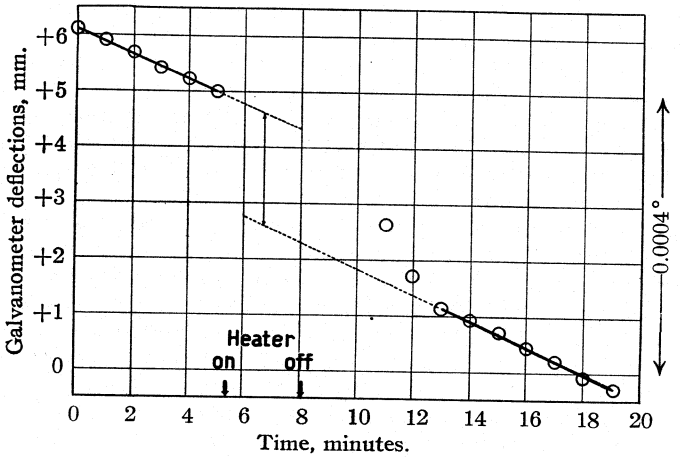


Fig. 2.—A typical experiment (LiCl, Experiment 1a).

can be seen, the deviations of the observed points from the straight lines are only of the order of 1 or 2 one hundred thousandths of a degree, and the lines before and after the experiment are nearly parallel. These facts make it possible to determine the actual temperature change during the experiment to better than one ten thousandth of a degree.

Two series of water standardizations were carried out in the manner previously described.[11] In the first series, 250.00 g. of water in the *tare*

[9] With the new type of heaters, a constant trend was reached about *five minutes* after the current was turned off, instead of *ten minutes* afterward as with the old coils (*cf.* Ref. 2, p. 1013).

[10] The advantage of this method, which has been used by a number of investigators, was pointed out to us by Dr. Malcolm Dole, who was able to obtain better agreement in measuring heats of dilution in this way. *Cf.* Richards and Dole, THIS JOURNAL, 51, 799 (1929).

[11] *Cf.* Ref. 2, p. 1011.

calorimeter was balanced against weights of water in the *working* calorimeter which were varied from 250.40 to 250.66 g. (*in vacuo*). In order to accommodate the thermally equivalent weight of the concentrated solutions of low specific heat, a second series of standardization experiments was made with 15 g. less water in each calorimeter. The two series are plotted in Fig. 3.[12] The radius of the circle marking each point will be

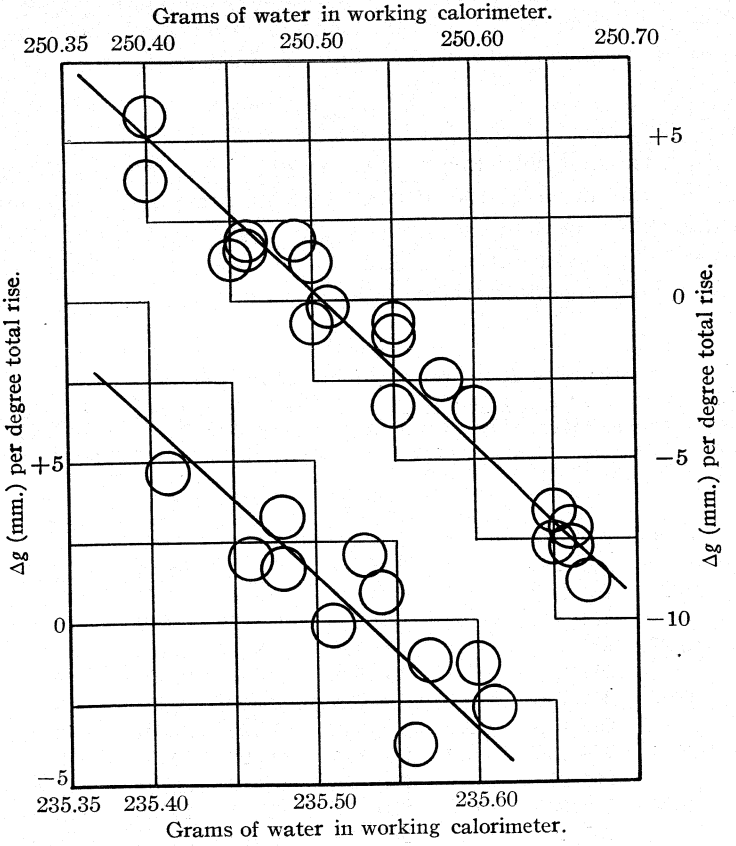


Fig. 3.—Calibration curves.

seen to represent a deviation of 0.005%, and the concordance of the results can be judged from the figure. Enough experiments were made, at in-

[12] After a few preliminary water experiments were made to develop the experimental technique, no experiments with water or solution were rejected except those affected by some known cause of error and two early standardizations made June 10, 1930. In these, 250.41 g. of water (*in vacuo*) gave corrected galvanometer deflections of +0.8 and +0.5 mm. These results differed by about 0.03% from the calibration curve based on all other results and hence were rejected, on the assumption that some large error (such as 0.1 g. in weighing) was responsible for the discrepancy. Even if these results were included, however, the curve would not be greatly affected.

tervals during the course of the work, to reduce the probable error in the water value to about ±0.005%—half that desired in the case of any individual solution. The exact cause of the small residual uncertainty is not known, but further repetition would have served no useful purpose.

## Results

The results are summarized in the accompanying Tables I–III.

Beside the values of the specific heats are tabulated those of the apparent molal heat capacity of the solute, defined as

$$\Phi = \left[\frac{1000}{m} + M_2\right]s - \frac{1000}{m}$$

where $M_2$ is the molecular weight of the solute. $\Phi$ is given in 25°-calories/degree, the unit in which the specific heats are measured. This quantity, which was shown by Randall and Rossini[13] to vary directly with $\sqrt{m}$ over a wide range of concentrations and for a large number of salts, is extremely useful in tabulating specific heat data. As was pointed out by Rossini,[14]

TABLE I[a]

SUMMARY OF RESULTS FOR LITHIUM CHLORIDE SOLUTIONS

The quantities of water and of solution were weighed out to even centigrams (±2 mg.). All weights are *in vacuo*. $\Delta g$ is the corrected galvanometer deflection for 1° total rise. The specific heat, $s$, is referred to water at the same temperature as unity, hence values of $\Phi$ are in 25°-calorie units.

| Expt. | $m$ | Solution, g. | $\Delta g$, mm. | Equiv. wt. of water | Specific heat, $s$ | Mean temp., °C. | $\Phi$ | $\sqrt{m}$ |
|---|---|---|---|---|---|---|---|---|
| 5a | 0.0400 | 251.080 | +0.6 | 250.494 | 0.99767 | 25.02 | −15.9 | 0.200 |
| b | | 251.110 | − .1 | 250.508 | .99760 | 24.96 | −17.7 | |
| 8a | .0625 | 251.390 | −1.4 | 250.535 | .99660 | 25.00 | −13.3 | .250 |
| b | | 251.340 | +0.2 | 250.503 | .99667 | 25.01 | −12.2 | |
| 4a | .0897 | 251.780 | +1.0 | 250.486 | .99486 | 25.01 | −15.1 | .299 |
| b | | 251.810 | −0.1 | 250.508 | .99483 | 25.01 | −15.5 | |
| 7a | .1600 | 252.770 | − .7 | 250.521 | .99110 | 25.01 | −13.6 | .400 |
| b | | 237.610 | +1.7 | 235.494 | .99109 | 25.01 | −13.7 | |
| 3a | .2504 | 254.020 | −0.4 | 250.514 | .98620 | 24.99 | −13.3 | .500 |
| b | | 253.970 | + .5 | 250.496 | .98632 | 25.01 | −12.8 | |
| 2a | .4904 | 257.360 | −6.0 | 250.629 | .97385 | 24.98 | −12.0 | .700 |
| b | | 257.190 | +1.1 | 250.483 | .97392 | 25.02 | −11.9 | |
| 1a | 1.0000 | 263.910 | −2.0 | 250.548 | .94937 | 25.00 | −10.38 | 1.000 |
| b | | 263.840 | +0.4 | 250.498 | .94943 | 25.00 | −10.31 | |
| c | | 263.820 | + .8 | 250.490 | .94947 | 25.02 | −10.27 | |
| 6a | 2.4614 | 264.940 | ± .0 | 235.530 | .88899 | 25.03 | − 7.41 | 1.569 |
| b | | 264.970 | −1.0 | 235.552 | .88898 | 25.01 | − 7.41 | |

[a] The experiments are numbered in chronological order. $m$ is moles of solute per 1000.0 g. of water. The atomic weights are those of the 1930 report, THIS JOURNAL, **52**, 861 (1930).

[13] Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

[14] F. D. Rossini, "Heat Capacities in Some Aqueous Solutions," Research Paper No. 151, reprinted from *Bur. Standards J. Research*, **4**, 315 (1930).

TABLE II

SUMMARY OF RESULTS FOR HYDROCHLORIC ACID SOLUTIONS

| Expt. | $m$ | Solution, g. | $\Delta g$, mm. | Equiv. wt. of water | Specific heat, $s$ | Mean temp., °C. | $\Phi$ | $\sqrt{m}$ |
|---|---|---|---|---|---|---|---|---|
| 5a | 0.0100 | 250.670 | −3.8 | 250.584 | 0.99966 | 24.99 | + 2.5 | 0.100 |
| b | | 250.570 | +2.8 | 250.448 | .99951 | 25.00 | −12.5 | |
| c | | 250.620 | +0.6 | 250.494 | .99950 | 25.00 | −13.5 | |
| d | | 250.600 | +1.6 | 250.473 | .99949 | 25.00 | −14.5 | |
| 4a | .0400 | 251.150 | −2.5 | 250.557 | .99764 | 25.00 | −22.6 | .200 |
| b | | 251.030 | +3.8 | 250.427 | .99760 | 24.99 | −23.6 | |
| 8a | .0626 | 251.490 | −0.3 | 250.513 | .99612 | 25.00 | −25.7 | .250 |
| b | | 251.460 | + .8 | 250.492 | .99615 | 25.00 | −25.2 | |
| 3a | .0900 | 251.960 | − .6 | 250.518 | .99428 | 24.99 | −27.3 | .300 |
| b | | 252.040 | −3.7 | 250.582 | .99422 | 24.99 | −27.9 | |
| 2a | .1629 | 253.140 | −0.8 | 250.523 | .98966 | 24.98 | −27.4 | .404 |
| b | | 253.250 | −3.7 | 250.582 | .98946 | 24.96 | −28.6 | |
| c | | 253.060 | +3.3 | 250.438 | .98964 | 24.99 | −27.5 | |
| 1a | .2552 | 254.530 | +1.7 | 250.472 | .98406 | 25.08 | −26.5 | .505 |
| b | | 254.630 | −4.9 | 250.607 | .98420 | 25.00 | −26.0 | |
| c | | 254.580 | −2.8 | 250.564 | .98422 | 24.99 | −25.9 | |
| 7a | .8100 | 247.430 | −0.5 | 235.508 | .95182 | 25.00 | −24.77 | .900 |
| b | | 247.390 | +1.4 | 235.474 | .95183 | 24.99 | −24.76 | |
| 6a | 2.0112 | 264.480 | +3.5 | 235.437 | .89019 | 24.98 | −22.13 | 1.418 |
| b | | 264.580 | −2.6 | 235.545 | .89026 | 25.01 | −22.10 | |

TABLE III

SUMMARY OF RESULTS FOR POTASSIUM HYDROXIDE SOLUTIONS

| Expt. | $m$ | Solution, g. | $\Delta g$, mm. | Equiv. wt. of water | Specific heat, $s^b$ | Mean temp., °C. | $\Phi$ | $\sqrt{m}$ |
|---|---|---|---|---|---|---|---|---|
| 5a | 0.0399 | 236.310 | −2.1 | 235.574 | 0.99687 | 25.02 | −23 | 0.200 |
| b | | 251.290 | −1.8 | 250.543 | .99697 | 24.97 | −21 | |
| 8a | .0622 | 251.760 | +0.2 | 250.502 | .99500 | 24.99 | −25 | .249 |
| b | | 236.680 | +1.4 | 235.500 | .99501 | 25.02 | −25 | |
| 6a | .0894 | 252.390 | −1.4 | 250.536 | .99268 | 25.00 | −27 | .299 |
| b | | 252.800 | −3.4 | 250.574 | .99272 | 25.04 | −26 | |
| 7a | .1602 | 253.800 | +1.7 | 250.472 | .98690 | 25.00 | −27.0 | .399 |
| b | | 253.760 | +3.4 | 250.436 | .98692 | 25.02 | −27.0 | |
| 2a | .2497 | 240.370 | −0.4 | 235.516 | .97978[1] | 25.02 | −25.9 | .500 |
| b | | 255.640 | + .8 | 250.490 | .97982 | 25.01 | −25.7 | |
| 3a | .4931 | 244.830 | + .5 | 235.496 | .96183[2] | 25.02 | −23.4 | .702 |
| b | | 260.280 | +5.7 | 250.429 | .96190 | 25.01 | −22.7 | |
| 1a | .8484 | 250.930 | +5.6 | 235.411 | .93803[3] | 25.01 | −20.4 | .921 |
| b | | 267.070 | −1.2 | 250.534 | .93799 | 25.04 | −20.4 | |
| 4a | 2.5873 | 277.200 | −11.8[a] | 235.286 | .84845[4] | 25.02 | −11.00 | 1.609 |
| b | | 277.500 | +1.1 | 235.512 | .84837 | 25.02 | −11.03 | |

[a] Calibration curve extends only to −6.7 mm. The equivalent weight of water in this case was obtained by linear extrapolation.

[b] Correction was made for 0.74 mole per cent. $Na^+$ from the data of Richards and Rowe.[15] Assuming linear change of $s$ with mole per cent. at any one concentration of $OH^-$ the corrections were: [1] $3 \times 10^{-4}$ calorie/degree; [2] $7 \times 10^{-4}$ calorie/degree; [3] $12 \times 10^{-4}$ calorie/degree; [4] $35 \times 10^{-4}$ calorie/degree.

[15] Richards and Rowe, THIS JOURNAL, 43, 770 (1921).

it "gives directly the relatively small difference between the heat capacity of a given amount of solution and the heat capacity of an amount of pure water equivalent to that in the given solution." The convenience of $\Phi$ is shown by the following illustration: Wanting to know the specific heat of 1 $m$ lithium chloride when starting our series of experiments, we plotted the values of $\Phi$ against $\sqrt{m}$ for lithium chloride solutions at 18° from the data of Richards and Rowe[15] and thus determined the best smoothed value of $\Phi$ when $m = 1$. This value, $-12.3$, was corrected to 25° by the temperature coefficient of $\Phi$ between 18 and 25°, found by combining the data of Richards and Rowe for sodium chloride and potassium chloride with those of Randall and Rossini for the same salts. This gave $\Phi = -10.6$ and $s = 0.94916$. Our direct experiments gave $s = 0.94942$ (slightly less than 0.03% different) and $\Phi = -10.3$.

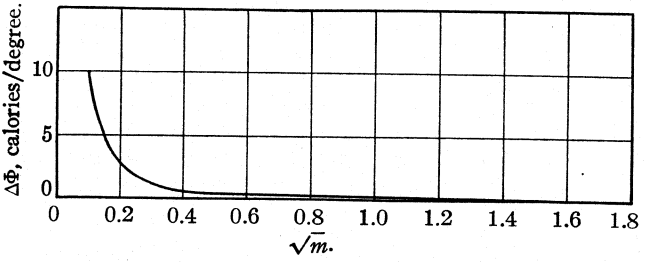


Fig. 4.—Error in $\Phi$ for 0.01% error in $s$.

The usual method of differentiating for errors shows how the values of $\Phi$ are affected by errors in $m$ and in $s$.

$$\Delta\Phi = \frac{1000}{m}(1-s)\frac{\Delta m}{m}$$

$$\Delta\Phi = \left[\frac{1000}{m} + M_2\right]\Delta s \simeq \frac{1000}{m}\frac{\Delta s}{s}$$

Since over a wide range $(1-s)$ decreases almost exactly as fast as $(1000/m)$ increases, their *product* has a constant value of about 50. An error of 0.1% in $m$ therefore only causes an error of 0.05 calorie per degree in $\Phi$. On the other hand, the error in $\Phi$ caused by any error in $s$ is *inversely proportional* to $m$. An error of 0.01% in $s$ changes the value of $\Phi$ by only 0.04 in a 2.5 $m$ solution but by 10 in a 0.01 $m$ solution. This makes it useless to go below 0.04 or 0.01 $m$ in these experiments. In Fig. 4 is shown the effect upon $\Phi$ of a 0.01% error in $s$. The error is plotted against $\sqrt{m}$ so as to be comparable with the other curves. In all but the most concentrated solutions, the limiting factor is the error in $s$, if that in $m$ is 0.1%. Even at 2.25 $m$ an error of 0.01% in $s$ is three times as serious as one of 0.03% in $m$.

Figures 5 and 6 show graphically the results for $\Phi$ plotted against $\sqrt{m}$. Experimental values are indicated by separate circles or triangles. Several concentric marks indicate coincident results. Three series of experiments

are distinguished in the lithium chloride results by means of signs within the circles. The more dilute solutions in each series were made by quanti-

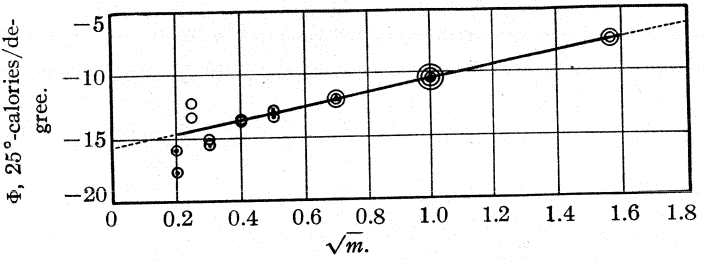


Fig. 5.—Apparent molal heat capacity of lithium chloride.

tative dilution of the most concentrated, which was analyzed as previously described.

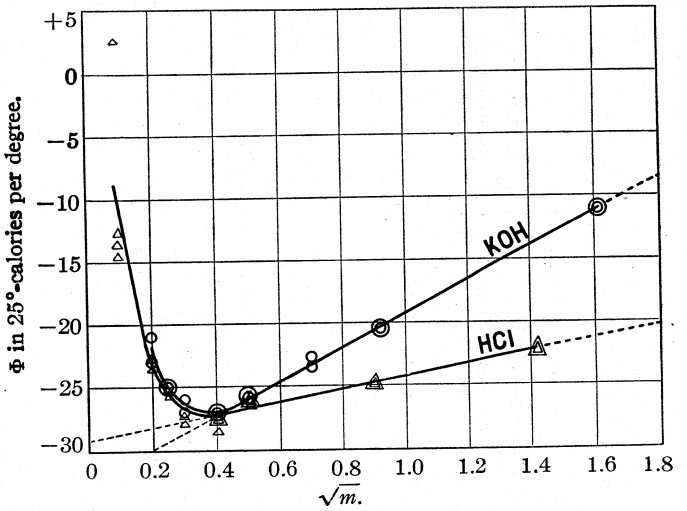


Fig. 6.—Apparent molal heat capacity of solute.

From the values of Φ it is a simple matter to calculate the partial molal heat capacity of the solute ($\overline{C}_{p_2}$) and the relative partial molal heat capacity of the solvent ($\overline{C}_{p_1} - \overline{C}^{\circ}_{p_1}$) by the method used by Randall and Rossini,[16] using the equations

$$\overline{C}_{p_2} = \Phi + {}^1/_2\, m^{1/2}\left(\frac{d\Phi}{dm^{1/2}}\right) \quad \text{and}$$

$$\overline{C}_{p_1} - \overline{C}^{\circ}_{p_1} = -\frac{m}{55.507}\left({}^1/_2\, m^{1/2}\,\frac{d\Phi}{dm^{1/2}}\right)$$

The values of these quantities are shown graphically in Figs. 7 and 8. In Table IV are given values of Φ, $\overline{C}_{p_2}$ and $\overline{C}_{p_1} - \overline{C}^{\circ}_{p_1}$ for rounded values of the concentration.

[16] Randall and Rossini, THIS JOURNAL, 51, 323 (1929).

TABLE IV

SUMMARY OF RESULTS FOR ALL SOLUTIONS AT ROUNDED CONCENTRATIONS

(Figures in parentheses are extrapolated)

| | Molality, $m$ | 0.01 | 0.04 | 0.10 | 0.25 | 0.50 | 0.75 | 1.00 | 1.25 | 1.50 | 1.75 | 2.00 | 2.25 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $-\Phi = 15.63-5.25\,m^{1/2}$ | (15.1) | 14.6 | 14.0 | 13.0 | 11.9 | 11.1 | 10.38 | 9.76 | 9.20 | 8.69 | 8.21 | 7.76 |
| LiCl | $-\bar{C}_{p_2} = 15.63-7.88\,m^{1/2}$ | (14.8) | 14.1 | 13.1 | 11.7 | 10.1 | 8.8 | 7.75 | 6.82 | 6.09 | 5.23 | 4.50 | 3.81 |
| | $-100(\bar{C}_{p_1}-\bar{C}^{\circ}_{p_1}) = 4.68\,m^{3/2}$ | (0.005) | 0.04 | 0.15 | 0.58 | 1.65 | 3.04 | 4.68 | 6.53 | 8.59 | 10.82 | 13.23 | 15.78 |
| | $-\Phi = 29.20-5.00\,m^{1/2}$ [a] | 9 | 23 | 27.0 | 26.7 | 25.7 | 24.9 | 24.20 | 23.62 | 23.08 | 22.59 | 22.13 | (21.70) |
| HCl | $-\bar{C}_{p_2} = 29.20-7.50\,m^{1/2}$ [a] | 17 | 30 | 29 | 25.5 | 23.9 | 22.7 | 21.70 | 20.82 | 20.02 | 19.26 | 18.60 | (17.95) |
| | $-100(\bar{C}_{p_1}-\bar{C}^{\circ}_{p_1}) = 4.50\,m^{3/2}$ [a] | −0.13 | −0.50 | −0.36 | 0.56 | 1.59 | 2.93 | 4.50 | 6.29 | 8.25 | 10.40 | 12.73 | (15.20) |
| | $-\Phi = 32.10-13.25\,m^{1/2}$ [a] | (9) | 22 | 26.1 | 25.5 | 22.7 | 20.6 | 18.75 | 17.29 | 15.87 | 14.57 | 13.34 | 12.21 |
| KOH | $-\bar{C}_{p_2} = 32.10-19.88\,m^{1/2}$ [a] | (17) | 29 | 30.2 | 22.3 | 18.0 | 14.9 | 12.22 | 10.90 | 7.75 | 5.79 | 3.96 | 2.30 |
| | $-100(\bar{C}_{p_1}-\bar{C}^{\circ}_{p_1}) = 11.99\,m^{3/2}$ [a] | (−0.13) | −0.47 | −0.73 | 1.49 | 4.25 | 7.73 | 11.89 | 16.65 | 21.86 | 27.62 | 34.22 | 40.25 |

[a] These expressions are valid above $m = 0.2$. The entries in the table are the best values, corresponding to the curves of Figs. 5, 6, 7 and 8.

## Discussion

The results obtained for the lithium chloride solutions are about what would be predicted. Over the whole range from 2.46 *m* to 0.04 *m* the values of Φ plotted against $\sqrt{m}$ fall along a straight line, from which they deviate only in the very dilute range. In no case does this deviation correspond to one in *s* appreciably greater than 0.01%. When correction is made for the difference in temperature, as previously explained, our results are in excellent agreement with those of Richards and Rowe and of Jauch (both at 18°) which have been plotted by Rossini.[17]

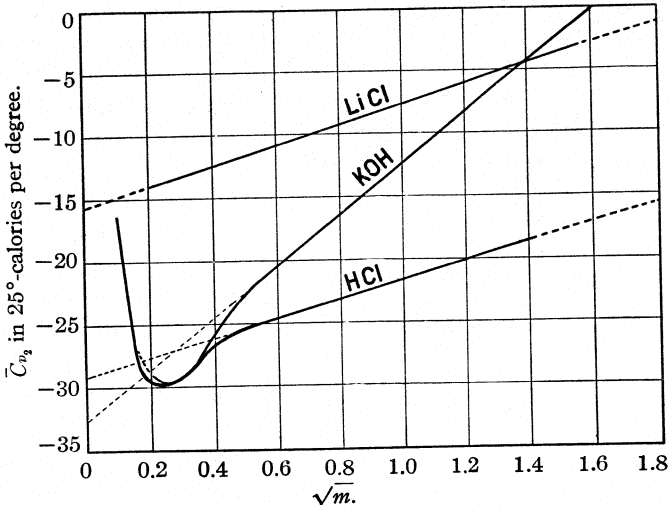


Fig. 7.—Partial molal heat capacity of solute.

The results obtained with hydrochloric acid and potassium hydroxide above about 0.2 *m* also show the expected absolute linearity of Φ against $\sqrt{m}$. In the very dilute range, however, they are more interesting. Both curves show sudden breaks and a decided *increase* in the apparent molal heat capacity as the dilution is increased. There seems to be no indication of such a change in any previous work, with the possible exception of lithium hydroxide at 18° as plotted by Rossini from the data of Richards and Rowe. Their data are not sufficiently precise to be conclusive and we are now studying solutions of lithium hydroxide and sodium hydroxide in this Laboratory to see if they behave like potassium hydroxide. Although the deviation we find is only about twice the probable experimental error, fourteen experiments show this deviation, while none deviates in the

[17] F. D. Rossini, "Apparent and Partial Molal Heat Capacities in Aqueous Solutions of Nineteen Uni-univalent Strong Electrolytes," Research Paper No. 331, reprinted from *Bur. Standards J. Research*, **7**, 47 (1931).

other direction. Moreover, nearly the same curve is followed by the two solutions, which seem to behave very similarly. Most of the results with hydrochloric acid were obtained consecutively by the senior author. After this, the perfectly linear ones for lithium chloride were found and then those for potassium hydroxide by the junior author. Finally a new solution of 0.0626 *m* hydrochloric acid was made up, standardized and investigated. The results (Experiments 8a and b) are seen to fall exactly on the curve previously plotted. This self-consistency and agreement with the results obtained five months or more before seems to indicate that the effect is not due to experimental error. Moreover, as the apparatus is standardized with water and is strictly differential, we should expect any systematic error to disappear at great dilution. That due to the different cooling by evaporation from the surface of the water and from that of the solution,[18] into the small air space above the liquid, is known to be negligible even at the highest concentrations. The volume of the air space was only 42 cc. and the evaporation from the *water*, due to the increased vapor pressure during an experiment, was found to amount to only $1.3 \times 10^{-4}$ degree per degree total rise. The difference in the case of the solution is therefore entirely negligible.

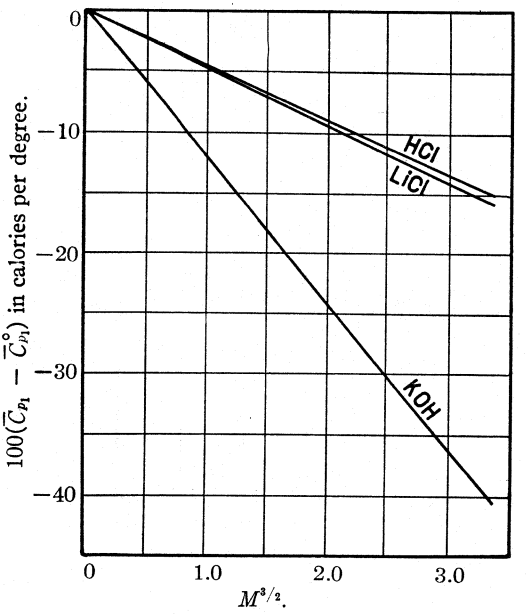


Fig. 8.—Relative partial molal heat capacity of solvent.

It is impossible to follow the course of the apparent molal heat capacity curves to any lower concentration by specific heat measurements with our present apparatus; nor does it seem promising to try to push the accuracy of these measurements beyond the limit of 0.01% in our experiments and those of Randall and Rossini. However, it should be possible to determine apparent molal heat capacities in even more dilute solutions from the heats of dilution at two different temperatures.[19] The very small temperature changes due to dilution can be measured with extreme calorimetric

[18] Ref. 2, p. 1014.

[19] This method has been used frequently; recently with great success by Richards and his co-workers, THIS JOURNAL, **51**, 707 *et seq.* (1929).

*sensitivity* without requiring a high *percentage* accuracy. We are now setting up an apparatus to measure the heats of dilution of such solutions with a sensitivity of $10^{-6}$ degree, as Lange and his co-workers have done, mostly at one temperature, for the last few years.[20]

Our results for hydrochloric acid agree well with those of Richards, Mair and Hall,[21] corrected from 18 to 25° as before. Their results for the most concentrated solutions were obtained directly, while those for the more dilute ones were calculated from the temperature coefficient of the heats of dilution. They are appreciably *higher* than those of Randall and Ramage[22] who obtain an extrapolated value of $-42$ calories per degree for $\overline{C}_{p_2}^{\circ}$, compared with our value of $-28$, from linear extrapolation of the values for $\Phi$ from 0.09 $m$ and higher. The much greater scattering of their experimental points for $\overline{C}_{p_2}$ over the whole range of $\sqrt{m}$ is doubtless due in great measure to the use of a method of calculating the partial molal heat capacity which is inferior to that used by Randall and Rossini; but their data seem less accurate than those of the latter.

The results for potassium hydroxide are in good agreement with those of Richards and Rowe and Richards and Hall, as plotted by Rossini.[23]

Our results at low concentrations show that the extrapolation of the apparent molal heat capacity curves to infinite dilution is a much more dubious procedure than was formerly realized, at least in the case of *strong* electrolytes. Rossini[24] postulated abrupt changes in the apparent molal heat capacity of *weak* electrolytes in the range below 0.04 $m$, in order to account for the discrepancy between the extrapolated curve for such a substance as citric acid (which he concludes represents nearly the apparent molal heat capacity of the *undissociated* substance) and the value calculated from the sum of the values for the individual ions. These values for individual ions are obtained and combined in a manner similar to that used to determine the value of $\Lambda_\infty$ for a weak electrolyte by Kohlrausch's law. We have no criticism of the conception that in very dilute solutions the apparent molal heat capacity of the ions must be additive, but we doubt if it is possible to extrapolate safely even from a concentration as low as 0.04 $m$, in order to obtain the limiting values. La Mer and Cowperthwaite[25] have reached the same conclusion. From a study of the e. m. f. of suitable cells over a wide range of temperature, they have calculated $\overline{C}_{p_2}$ for zinc sulfate below 0.01 $m$ and find that, even as low as 0.0005 $m$, it is not a linear

[20] Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931), summarizes this excellent work.

[21] Richards, Mair and Hall, THIS JOURNAL, **51**, 727 (1929).

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

[23] Ref. 17, p. 50.

[24] F. D. Rossini, Ref. 14, p. 323.

[25] Paper presented before the Buffalo meeting of the American Chemical Society by La Mer. The experimental work has been published in Cowperthwaite's Thesis, Columbia University, 1930.

function of $\sqrt{m}$. "This shows how misleading it is to extrapolate calorimetric data linearly from 0.01 or 0.02 *m* to zero concentration."

The incorrectness of such a procedure in the case of heats of dilution has been shown by Lange's work in the very dilute range. Even such a salt as potassium nitrate, which *absorbs* a great deal of heat on dilution to 0.04 *m*, is found to *give out* heat on dilution below 0.01 *m*. This is strikingly shown by a comparison of the heats of dilution of many strong electrolytes down to moderate dilution, measured by Richards and Rowe, with those of similar electrolytes in the extremely dilute range, measured by Lange and his co-workers. Such a graphical comparison has been made by one of us.[26]

Moreover, it seems impossible to account for the linear change of the apparent and partial molal heat capacities with $\sqrt{m}$ *up to a concentration of several molal* by an application of the Debye–Hückel limiting law, as did Randall and Rossini. This would mean that the *second derivative* of the partial molal electrical free energy was correct at a concentration where the function and first derivative (measured by the logarithm of the activity coefficient and the partial molal heat content) no longer were applicable. The experimental curves have appreciably different slopes over the range studied and all are about *three times* that predicted by the theory. Also, if they are actually linear in the dilute range, there is no chance for them to approach a *common* limiting tangent. Finally, as Randall and Rossini observe, a negative value for the partial molal heat capacity *at infinite dilution* is inexplicable on the Debye–Hückel theory, since charged ions, infinitely far apart, have no effect on each other. Such a negative value, if it really is the limiting one, must seek an explanation in the effect of the ions upon the solvent molecules, such as has been postulated by Zwicky.[27] His calculation of the apparent molal heat capacity in dilute solutions, however, gives a negative value which is about four times that actually observed.

Further study of the heat capacity of solutions of strong electrolytes in very dilute solutions, such as we are preparing to carry out, should at least provide experimental data by which any theoretical explanation must finally be gaged.

It is a pleasure to acknowledge once again our indebtedness to Professor A. A. Noyes for the kind gift of the apparatus built at the California Institute of Technology, and to an anonymous benefactor of the Wolcott Gibbs Memorial Laboratory of Harvard University for financial aid in the improvements in the apparatus made at that time.

## Summary

The adiabatic twin calorimeter method of determining specific heats of aqueous solutions has been further improved and used to determine the

[26] Gucker, *School Science and Mathematics*, **29**, 929, 930 (1929).

[27] F. Zwicky, *Physik. Z.*, **27**, 271 (1926), summarized in *Physik. Z.*, **26**, 664 (1925); and *Proc. Nat. Acad. Sci.*, **12**, 86 (1926).

heat capacities of aqueous solutions of lithium chloride, hydrogen chloride and potassium hydroxide at 25°. The solutions have been investigated from a concentration of 0.01 or 0.04 *m* to a concentration of 2 to 2.5 *m*, with a precision of about 0.01%.

The apparent molal heat capacity of the solutes plotted against the square root of the molality shows the important linear relation announced by Randall and Ramage and confirmed by Randall and Rossini: in the case of lithium chloride solutions over the whole concentration range and in the case of the other solutions *above* about 0.2 *m*. In the range *below* this concentration, however, the apparent molal heat capacity shows a sudden *increase* which has not been noted before. This throws some doubt on the validity of extrapolation to infinite dilution. Work is now in progress in this Laboratory to see if this behavior is shown by other solutions.

The partial molal heat capacities of the solute and those of the solvent have been calculated and are presented in graphs and tables.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 89]

# THE SORPTION OF GASES BY COPPER

BY ARTHUR F. BENTON AND T. A. WHITE[1]

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## Introduction

The numerous researches of recent years on the adsorption of gases by solids possessing catalytic activity have brought to light many cases in which gas is extensively and strongly adsorbed at relatively high temperatures and low pressures, where the older idea of adsorption as merely an increased concentration of ordinary molecules at the solid surface would predict that little or no gas would be taken up. These anomalous adsorptions were variously described as "selective," "irreversible," "chemical," etc. Nevertheless the idea persisted that such processes differed only in degree from "physical" adsorption,[2] and that no sharp distinction could be drawn.

As a result of an extensive investigation of the adsorption of gases by oxide catalysts, Benton[3] proposed the view that the two kinds of adsorption could be sharply differentiated, and that the total adsorption by active solids was the sum of the amounts of gas taken up in the two different ways.

[1] Du Pont Fellow in Chemistry.

[2] See, for example, Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 2d ed., p. 193 (1929).

[3] Benton, THIS JOURNAL, **45**, 887, 900 (1923). This work was carried out in the Princeton Laboratory, with the coöperation and advice of Professor H. S. Taylor.

A simple method was found for estimating these separate quantities, based on a comparison of the adsorption ratios of pairs of gases by a number of surfaces of widely differing catalytic activity.

Definite proof of the separate existence of the two types of adsorption was obtained by Benton and White[4] in the system nickel–hydrogen. They found that the physical adsorption occurring at low temperatures decreased rapidly from −210 to −183°; at higher temperatures this type was superseded by "chemical," or "activated" adsorption, characterized by very strong binding forces. Subsequently, the same phenomena were observed in other systems.[5]

Taylor[6] has recently presented an extensive survey of the available information on activated adsorption, and has particularly emphasized the slow rate of this process and the increase of rate with temperature, as interpreted in terms of an "activation energy" of adsorption. While a slow rate, increasing with temperature, is a very important characteristic of activated adsorption, as distinguished from the physical type, rate alone does not distinguish it from other slow processes, such as compound formation and solubility. Some workers, overlooking the fact that activated adsorption may often be recognized by a characteristic type of equilibrium, high heat of adsorption, etc., independently of rate phenomena, have attempted to interpret all such slow processes as solubility, and have thus been led to question the existence of activated adsorption.[7]

The present paper contains the results of an extended investigation of the adsorption of nitrogen, hydrogen and carbon monoxide by two samples of reduced copper, at pressures up to one atmosphere and at temperatures extending down to 78°K. Although the adsorption of nitrogen under the conditions studied is purely of the physical type, hydrogen exhibits all three of the processes mentioned above, namely, physical adsorption, activated adsorption and solubility. The amounts of hydrogen taken up in each of the three ways have been separately determined. Carbon monoxide also shows three different processes, two of which are readily distinguishable as physical and activated adsorption. The third process is provisionally regarded as solution, but may well be a second type of activated adsorption.

Numerous studies of the sorption of gases by copper have previously been reported, among which may be mentioned the solubility measurements of Sieverts[8] at high temperatures, and the sorption experiments of

[4] Benton and White, THIS JOURNAL, **52**, 2325 (1930).

[5] Garner and Kingman, *Nature*, **126**, 352 (1930); Taylor and Williamson, THIS JOURNAL, **53**, 2168 (1931); Taylor and McKinney, *ibid.*, **53**, 3604 (1931).

[6] Taylor, *ibid.*, **53**, 578 (1931).

[7] Steacie, *J. Phys. Chem.*, **35**, 2112 (1931); Ward, *Proc. Roy. Soc.* (London), **A133**, 506, 522 (1931).

[8] Sieverts, *Z. physik. Chem.*, **77**, 591 (1911).

Taylor and Burns,[9] Pease,[10] Griffin[11] and Ward.[7] None of these investigations has extended to temperatures below 0°.

## Experimental Procedure and Materials

The procedure consisted in admitting a known volume of gas to an evacuated bulb containing the adsorbent and noting the pressures produced as a function of time until equilibrium was approximately reached. Then a further quantity of gas was introduced and the process repeated until equilibrium pressures of approximately one atmosphere were reached. Frequently this procedure was reversed, the pressure being observed after withdrawal of a portion of gas from the bulb.

The quantity of gas adsorbed at any time was obtained by subtracting from the total volume admitted the volume of unadsorbed gas in the free space. The latter was determined directly by measurements with carefully purified helium at a series of temperatures down to −78.5°. For temperatures below −78.5° the volume of gas in the free space was obtained by calculation from the experimental values at each of the higher temperatures. The close concordance of the values so calculated shows that helium is not appreciably adsorbed above −78.5°. The apparatus has been previously described.[4] No stopcocks were employed in the part of the apparatus communicating with the adsorbent.

Two samples of copper were employed. Both were prepared by reduction of the oxide with hydrogen *in situ*, the first for about forty-eight hours at 150–170°, the second for one hour at 170°, ten days at 115° and nine days at 130–140°. The weights of copper were 71.15 g. and 51.51 g., respectively, for Cu I and Cu II.

Between successive "runs" the adsorbent was evacuated with a Töpler pump for two hours, at 200° for Cu I, and 170° for Cu II.

A considerable proportion of the experiments consisted of check runs designed to test the reproducibility of the results. No change was found to occur in Cu II, check runs as much as six months apart giving values in close agreement. The reproducibility was less satisfactory for Cu I, and accordingly the data obtained for this sample will be used only in confirmation of the results obtained with Cu II.

All volumes are given in cc. at 0°, 760 mm., and all pressures in mm. of mercury at 0°.

## Results with Nitrogen

The isotherms obtained for nitrogen on Cu II are shown in Fig. 1, Curves 1, 2, 3. Curve 1a shows on a reduced scale the complete isotherm at −183°, the first part of which is given in Curve 1. Here as elsewhere in this paper points designated by open circles, triangles, etc., were obtained by proceeding from lower to higher pressures; solid black symbols indicate the reverse process. It was found in all experiments with nitrogen that equilibrium was established practically instantaneously, as shown by the fact that the first pressure reading, taken two to three minutes after admitting the gas, remained unchanged as long as twenty hours. Because of the absence of drift in the work with nitrogen, it was not considered important to approach equilibrium from both sides; where this was done, however, it will be seen that the values are in close agreement.

[9] Taylor and Burns, THIS JOURNAL, **43**, 1273 (1921).

[10] Pease, *ibid.*, **45**, 2296 (1923).

[11] Griffin, *ibid.*, **49**, 2136 (1927).

It is evident that the effects of pressure and temperature on the adsorption of nitrogen by copper are qualitatively similar to the results so frequently obtained in the adsorption of gases by charcoal and silica. The observed phenomena are typical of *physical*, or molecular, adsorption. Thus, (1) equilibrium is reached from either side practically instantaneously, (2) the isotherms do not appear to approach a saturation limit, (3) there is no adsorption at "zero" pressure, (4) at temperatures far

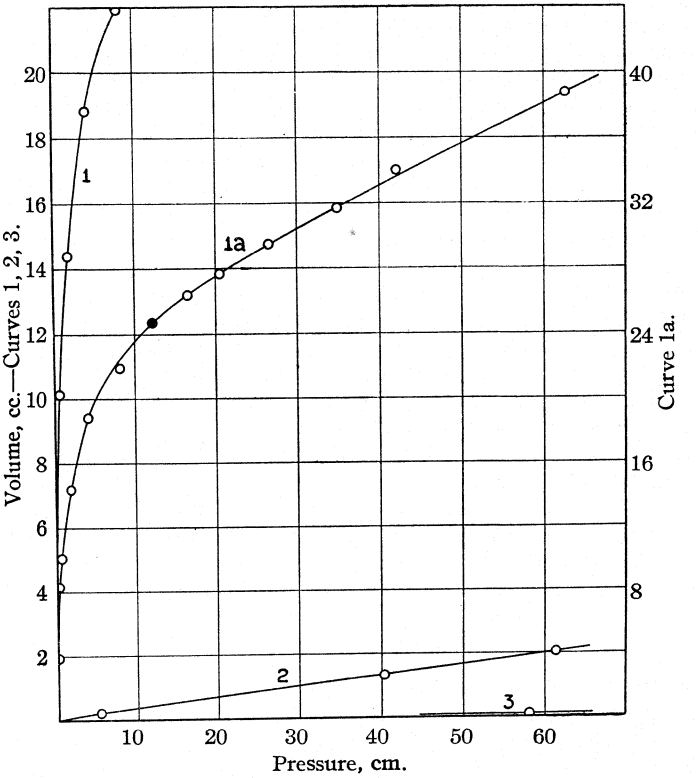


Fig. 1.—Isotherms for nitrogen: Curves 1 and 1a, −183°; Curve 2, −78.5°; Curve 3, 0°.

above the boiling point of nitrogen, the adsorption is approximately proportional to the pressure, (5) the adsorption at a given pressure decreases uniformly with rising temperature, (6) the heat of adsorption is relatively small. In the present case rough values of the heat of adsorption have been calculated from the Clausius–Clapeyron equation as follows. From an equation of the form $V = kp^{1/n}$, which agrees well with the data in the low-pressure part of Curve 1a, it was found that an adsorption of 2.0 cc. at −183° corresponds to a pressure of 0.0113 mm. By comparison of this value with the 604 mm. pressure in equilibrium with

2.0 cc. at −78.5°, the heat of adsorption was found to be 3600 cal. per mole. Another value was obtained by extrapolating Curve 2 on the assumption that at −78.5° the volume remains proportional to the pressure up to an adsorption of 10 cc., and comparing the pressures corresponding to this volume at the same two temperatures. The value thus obtained is 2100 cal. It may be concluded that the heats of adsorption on different parts of the copper surface range roughly from 4000 to 2000 cal., values which are, respectively, only three and one and one-half times the latent heat of vaporization of nitrogen at the boiling point (1380 cal.).

## Results with Hydrogen

**Isotherms at Low Temperatures.**—The values obtained for hydrogen on Cu II at low temperatures are shown in Fig. 2. If we omit from consideration the discontinuities in the adsorptions at −195 and −183°, a

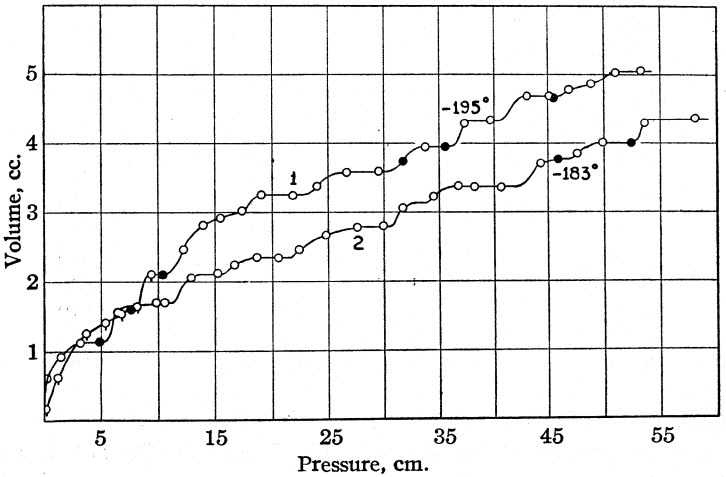


Fig. 2.—Isotherms for hydrogen at low temperatures.

detailed discussion of which has already been presented,[12] the curves at these two temperatures show all the ordinary characteristics of the physical type of adsorption. In both cases equilibrium was established practically instantaneously, and the values obtained were completely reversible, as may be seen from the close agreement of points obtained from higher and from lower pressures. Also, the adsorptions continue to increase rapidly with increasing pressure, without giving evidence of any approach to a saturation limit; at −183° the volume is nearly a linear function of the pressure. In general, the adsorption decreases with rising temperature, giving a heat of adsorption, as already reported,[12] of about 800 cal. for an adsorption of 2.5 cc., which falls to about 400 cal. as the volume

[12] Benton and White, THIS JOURNAL, 53, 2807, 3301 (1931).

taken up increases to 4.25 cc. Heats calculated for the first 1 or 2 cc. have no significance, since at −183° a slight adsorption, about 0.5 cc., occurs at "zero" pressure; this 0.5 cc., as will be shown below, is definitely to be attributed to adsorption of the chemical, or activated type, and hence is not comparable with the purely physical adsorption at −195°.

In an earlier experiment at −183° an isotherm was obtained which shows no adsorption at zero pressure, and which lies quite uniformly 0.5 cc. below Curve 2 of Fig. 2. It appears that for some reason the 0.5 cc. of activated adsorption did not occur in this case. The explanation is probably found in the fact that here the evacuated adsorbent was cooled for a longer period at −183° before the first admission of gas. While too few points were taken to trace out the detailed course of the isotherm, a heat of adsorption can be calculated from each observed point in conjunction with the corresponding point at −195°, as interpolated from Curve 1. The values thus obtained are listed in Table I.

TABLE I

HEAT OF PHYSICAL ADSORPTION OF HYDROGEN BY COPPER II

| Vol. adsorbed | $p$ at −195° | $p$ at −183° | $Q$ |
|---|---|---|---|
| 0.56 | 9 | 27.1 | 1280 |
| .83 | 18 | 64.7 | 1490 |
| 1.46 | 60 | 133.6 | 930 |
| 1.70 | 85 | 168.7 | 800 |
| 2.29 | 114 | 265.4 | 980 |
| 2.58 | 125 | 332.6 | 1140 |
| 3.33 | 229 | 421.4 | 710 |
| 3.54 | 255 | 486.6 | 750 |
| 3.68 | 315 | 508.7 | 560 |

It may be concluded that the heat of adsorption for the first few cc. of hydrogen is not far from 1000 cal. per mole. The latent heat of vaporization of hydrogen is about 220 cal. at the boiling point.

**Isotherms at Higher Temperatures.**—The adsorptions of hydrogen by Cu II at −78.5 and 0° are shown in Fig. 3, Curves 1 and 2. One of the most striking differences between these results and those given in the last section is that here equilibrium is approached with great slowness. In spite of the fact that for each point the pressure appeared to become constant after six to eight hours, it is clear that final equilibrium was not attained, since points obtained from the side of higher pressure give larger adsorptions than those obtained from the side of lower pressure. Nevertheless, the differences are not so great as to leave the general course of the isotherms in doubt. The curve at −78.5° is made up from all the points obtained in different runs; it was found that the longer the time of observation, the more closely Curve 1 was approached.

It is obvious that the process occurring at these temperatures differs

markedly from that at low temperatures. In addition to the great difference in rate, it is to be noted that here the isotherms tend to become comparatively flat at higher pressures, and that there is a large adsorption at zero pressure. Much more gas is taken up than at the low temperatures.

The results with Cu I completely paralleled those obtained with Cu II, except that in the former case the adsorptions were always smaller by a factor of about four.

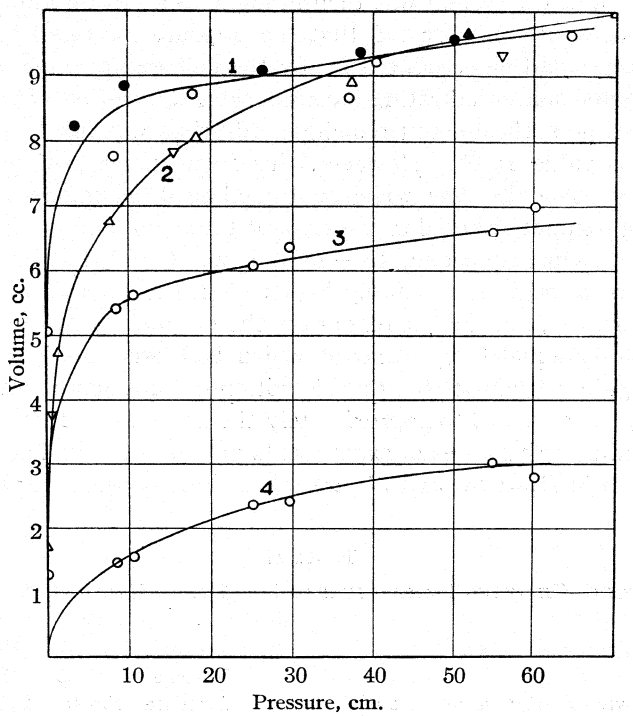


Fig. 3.—Isotherms for hydrogen: Curve 1, total sorption at −78.5°; Curve 2, total sorption at 0°; Curve 3, activated adsorption at 0°; Curve 4, solution at 0°.

**Experiments with Temperature Variation.**—With the adsorbent at −78.5° hydrogen was admitted and allowed to reach approximate equilibrium, 9.00 cc. being taken up at a pressure of 517.7 mm. In this condition the system was then cooled to −183° and an isotherm obtained at the latter temperature. It was found that the adsorption showed no tendency to decrease to the ordinary values at −183°, but on the contrary an immediate increase occurred. The excess over the 9 cc. originally present was nearly as great as the entire adsorption obtained directly at the low temperature. This experiment further shows that hydrogen is held at the higher temperature in a way fundamentally different from the physical

adsorption at −183°, and that the physical adsorptive capacity of the copper is somewhat, but not greatly, decreased by the presence of the large adsorption of the high temperature type, which remains on the surface upon cooling to the low temperature.

Similar experiments carried out between −78.5 and 0° reveal an entirely new situation. The procedure employed was as follows. The adsorbent was brought to approximate equilibrium with hydrogen at a given pressure at −78.5°, and the system was then brought to 0° as rapidly as possible. In this process it was observed that the pressure increased to an extent greater than could be accounted for by the change in temperature of the gas in the free space, indicating a considerable desorption of gas from the copper. In fact, the amount remaining adsorbed was much less than the equilibrium value at 0°. However, this large increase of pressure was followed by a slow decrease, which continued until the amount of gas taken up was approximately equal to the amount taken up in an ordinary experiment at 0°. On then cooling to −78.5° it was found that the adsorption increased to a value considerably higher than the original adsorption at this temperature, and this increase over the original value at −78.5° was approximately equal to the amount which had been slowly taken up at 0°. On again warming to 0°, the adsorption did not again pass through a minimum, but returned to approximately the usual value at 0°.

The results of this series of experiments are collected in Table II. The values given in Rows (3) and (7) are taken directly from Curves 2 and 1, Fig. 3.

TABLE II

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY CU II

| | | | Run no.....30 | 34 | 32 |
|---|---|---|---|---|---|
| (1) | Gas taken up at −78.5° | Pressure | 35.9 | 178.4 | 403.7 |
| | | Volume | 8.23 | 8.72 | 9.21 |
| (2) | Initial values after warming to 0° | Pressure | 105.0 | 295.6 | 602.3 |
| | | Volume | 5.64 | 6.37 | 7.00 |
| (3) | Total sorption at 0° at pressures given in (2) | | 7.20 | 8.80 | 9.80 |
| (4) | Difference of (2) and (3) | | 1.56 | 2.43 | 2.80 |
| (5) | Final values reached at 0° | Pressure | 84.5 | 251.3 | 550.2 |
| | | Volume | 6.59 | 8.40 | 9.40 |
| (6) | After cooling to −78.5° | Pressure | 22.5 | 139.7 | 355.3 |
| | | Volume | 9.07 | 11.18 | 12.23 |
| (7) | Direct values at −78.5° at press. given in (6) | | 7.60 | 8.80 | 9.20 |
| (8) | Difference of (6) and (7) | | 1.47 | 2.38 | 3.03 |

**Solubility of Hydrogen.**—In interpreting the facts shown in Table II it is necessary first to establish the source of the gas evolved in passing from −78.5 to 0°. The obvious possibility that this represents the normal decrease in the amount of gas *physically* adsorbed at −78.5° may be eliminated by the following reasoning. From the heat of physical ad-

sorption of hydrogen by Cu II, which was found above to be roughly 1000 cal. per mole, it is possible to calculate from each observed point at the low temperatures the pressure which would be in equilibrium with the same physical adsorption at $-78.5$ and at 0°. In this manner an isotherm can be constructed for the physical adsorption at each of these temperatures. The following values were thus obtained: for $p = 600$ mm., $V = 0.66$ cc. at $-78.5°$ and 0.44 cc. at 0°; for $p = 300$ mm., $V = 0.44$ cc. at $-78.5°$ and 0.31 cc. at 0°. Thus, at the highest pressure shown in Table II, the maximum amount of physically adsorbed gas which could be evolved in passing from $-78.5$ to 0° would be 0.22 cc., an amount which is almost negligible in comparison with the 2.8 cc. which was found actually to be evolved.

The assumption is justified, therefore, that the gas given up on warming to 0° is almost entirely composed of gas which was adsorbed in the activated form at $-78.5°$. The fact that after reaching 0° gas ceased to be evolved and resorption occurred, *shows clearly that a third kind of process takes place.* There can be little doubt that this represents a slow transfer of hydrogen into the interior of the copper. On cooling to $-78.5°$ this dissolved gas is unable to escape and remains "frozen" in the solid. At the same time, however, the activated adsorption on the surface resumes its normal value at $-78.5°$, so that the total "sorption" is greater than that originally obtained at this temperature.

If we assume for the moment that no solution occurs in an experiment carried out wholly at $-78.5°$, then the values shown in Row (2) of Table II represent the actual *ad*sorptions at 0°, while the differences in Row (4) are the volumes of gas *dissolved* at 0° at the pressures shown in Row (2). Similarly, the differences in Row (8) represent the volumes dissolved at 0° at the pressures given in Row (5). The values in Rows (3) and (5) are the sums of the adsorption and solution at 0°.

The amounts of gas dissolved at 0°, as given in Rows (4) and (8), have been plotted as Curve 4 of Fig. 3. It is not surprising to find that the volumes dissolved are approximately proportional to the square root of the pressure, a rule which has been found to hold for practically all measurements of the solubility of gases in solids.

When the dissolved gas is subtracted from the total taken up at 0°, Curve 3 of Fig. 3 is obtained, representing the actual adsorption at 0° plus any slight solution which may occur at $-78.5°$. The fact that Curves 1 and 3 are parallel to each other strongly suggests that there is in fact a slight solution at $-78.5°$. It is most probable that if this slight solubility, in amounts proportional to the square root of the pressure, were subtracted from Curves 1 and 3 to give the true adsorptions at $-78.5$ and 0°, both isotherms would reach definite saturation limits at pressures of 100–200 mm.

**Activated Adsorption of Hydrogen.**—The foregoing results show that when the solubility of hydrogen is subtracted from the total sorption, there remains an activated adsorption at −78.5 and at 0°, in comparison with which the physical adsorptions are almost negligibly small. The isotherms for activated adsorption are characterized by a large adsorption at very low pressures, and by a tendency to approach an early saturation limit.

A further distinguishing feature of activated adsorption is the comparatively slow rate at which equilibrium is established. In illustrating this point it is essential to select data obtained under conditions where the activated adsorption is not accompanied by the slow process of solution. Such conditions exist in the case of values obtained at very low pressures, and for the observations made after reaching equilibrium at 0° and then cooling to −78.5°. As representative of the rates observed under these conditions, Table III shows the rate data for (a) a low-pressure point at −78.5°, (b) a low-pressure point at 0° and (c) a point obtained at −78.5° after cooling from 0°. The values shown for zero time are the amounts taken up at the preceding point.

TABLE III

RATE OF ACTIVATED ADSORPTION OF HYDROGEN

| (a) −78.5° | | | (b) 0° | | | (c) −78.5° | | |
|---|---|---|---|---|---|---|---|---|
| Time, hrs. | *P* mm. | *V*, cc. | Time, hrs. | *P*, mm. | *V*, cc. | Time, hrs. | *P*, mm. | *V*, cc. |
| 0 | .. | 1.27 | 0 | .. | 1.70 | 0 | ... | 9.40 |
| 0.05 | 30.0 | 3.27 | 0.03 | 25.0 | 4.18 | 0.05 | 362.1 | 11.80 |
| 0.10 | 20.0 | 3.90 | 0.45 | 18.3 | 4.49 | 0.30 | 360.3 | 11.91 |
| 0.72 | 7.5 | 4.69 | 4.03 | 14.8 | 4.65 | 1.88 | 358.8 | 12.01 |
| 2.97 | 3.9 | 4.91 | 5.03 | 14.0 | 4.69 | 6.38 | 355.6 | 12.21 |
| 4.63 | 2.7 | 4.99 | 5.70 | 14.0 | 4.69 | 8.05 | 355.3 | 12.23 |
| 5.80 | 2.0 | 5.03 | | | | 9.63 | 355.3 | 12.23 |

It is evident that at −78.5° activated adsorption is a very slow process. At comparable pressures the rate is much faster at 0°, all but a few tenths of a cc. being taken up almost instantaneously. Comparison of (c) with (a) indicates that for values not too near equilibrium the rate at −78.5° is greater at higher pressures.

In Fig. 4 are shown a few of the data obtained for rates at higher pressures, both at −78.5° (Curves 1 and 2) and at 0° (Curves 3, 4, 5). The values given for zero time are the volumes taken up at the previous point. It is seen that in certain ranges hydrogen appears to be taken up *much more slowly at 0 than at −78.5°*. Closer observation shows, however, that the curves at −78.5° give a gradual and uniform decrease of rate, indicative of the single process of activated adsorption (solubility being practically negligible at this temperature), whereas at 0° two different processes are clearly disclosed, a very rapid activated adsorption, and a slow solution.

No attempt will be made in this paper to determine the various rates

as functions of pressure, temperature, amounts already sorbed, etc. It may be remarked, however, that when volume is plotted against the square root of the time, as in Fig. 4, the solution process yields lines which are nearly straight over a considerable range.

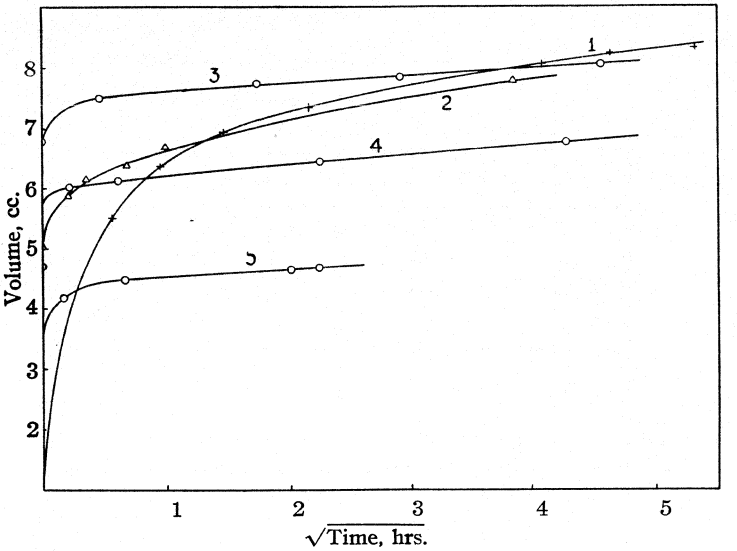


Fig. 4.—Rate of sorption of hydrogen: Curves 1 and 2, −78.5°; Curves 3, 4 and 5, 0°.

**Isobars for Hydrogen.**—The interrelationship of the solution process and the two types of adsorption on Cu II is brought out by Fig. 5, which represents the 500 mm. isobars for physical adsorption (Curve 2), for activated adsorption (Curve 3), and for the amount of solution which actually occurred in these experiments (Curve 4), which probably does not represent equilibrium. Curve 1, which is the sum of Curves 2, 3 and 4, gives the total sorptions observed experimentally.

## Results with Carbon Monoxide

**Isotherms.**—The data obtained for the isothermal adsorption of carbon monoxide by Cu II are plotted in Fig. 6, Curves 1, 2, 3, 4. Curve 1a shows on a reduced scale (at the right of the figure) the complete isotherm at −183°, the first part of which is given in Curve 1. The rate of adsorption at −183° was very rapid, a constant pressure being obtained within a few minutes after the admission of gas. Points approached from higher pressures agree well with those obtained from the side of lower pressure. At −78.5° (Curve 2) the rate was also rapid, and the points for adsorption and desorption are in satisfactory agreement. At 0° the major part of the

gas was adsorbed almost instantaneously, but this was followed by an extremely slow process in which small additional quantities of gas were taken up. The sum total of these small quantities for all the points amounted to 0.4 cc. Seven days were needed to complete the isotherm as shown in Curve 3. Although the final pressure at each point remained apparently constant for four to six hours, and the points obtained from

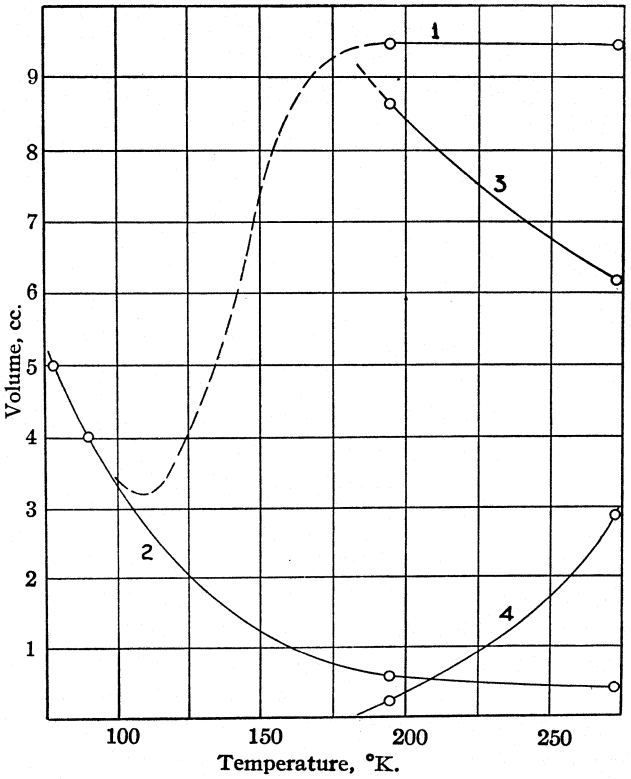


Fig. 5.—Isobars for hydrogen at 500 mm.: Curve 1, total sorption; Curve 2, physical adsorption; Curve 3, activated adsorption; Curve 4, solution.

higher and lower pressures agree well, it is possible that further sorption would have occurred if the times of observation had been greatly extended. At 110° there was again an almost instantaneous sorption, followed by a slow process. Here the slow process was considerably more rapid than at 0°, it involved much larger quantities of gas and equilibrium was definitely not reached even, in one case, after 280 hours. Of the 14.4 cc. taken up at the highest point in Curve 4, Fig. 6, about 7.0 cc. is accounted for by the slow process. The amounts taken up rapidly at 110° are plotted in Curve 5. Typical rate data are given in Table IV for some of the points at 0

and 110°. The values given for zero time are the final amounts taken up at the previous point.

TABLE IV

RATE OF SORPTION OF CARBON MONOXIDE

| 0° | | | | 110° | | | |
|---|---|---|---|---|---|---|---|
| Time, hr. | P, mm. | V, cc. | Rate, cc./hr. | Time, hr. | P, mm. | V, cc. | Rate, cc./hr. |
| 0 | ... | 0 | .. | 0 | ... | 0 | .. |
| 0.05 | 0 | 1.23 | .. | 0.05 | 2.0 | 1.82 | 36 |
| 0 | ... | 4.98 | .. | 0.80 | 1.3 | 1.84 | 0.03 |
| 0.03 | 26.0 | 9.23 | 140 | 1.9 | 1.3 | 1.84 | 0.00 |
| 0.82 | 25.0 | 9.28 | 0.064 | | | | |
| 3.83 | 24.0 | 9.33 | .017 | 0 | ... | 1.84 | .. |
| 20.0 | 23.5 | 9.35 | .001 | 0.02 | 50.6 | 4.68 | 140 |
| 27.0 | 23.0 | 9.37 | .003 | 0.92 | 43.0 | 4.94 | 0.29 |
| 33.0 | 23.0 | 9.37 | .000 | 17.2 | 16.5 | 5.81 | .053 |
| 0 | ... | 10.69 | .. | 25.2 | 12.5 | 5.95 | .018 |
| 0.08 | 377.0 | 11.36 | 8 | 39.9 | 8.5 | 6.08 | .009 |
| 16.7 | 376.0 | 11.41 | 0.003 | 63.7 | 6.0 | 6.16 | .003 |
| 24.4 | 375.0 | 11.46 | .006 | 72.7 | 5.0 | 6.19 | .003 |
| 36.2 | 374.8 | 11.47 | .000 | 90.7 | 4.3 | 6.22 | .002 |
| 41.4 | 374.9 | 11.46 | .000 | 95.9 | 4.0 | 6.23 | .002 |
| | | | 110° | | | | |
| 0 | ... | 6.23 | .. | 117.3 | 212.5 | 12.95 | 0.013 |
| 0.05 | 300.0 | 10.05 | 76 | 144.3 | 203.5 | 13.25 | .011 |
| 0.97 | 295.0 | 10.22 | 0.19 | 168.3 | 196.0 | 13.50 | .010 |
| 15.8 | 272.0 | 10.98 | .051 | 193.3 | 188.5 | 13.74 | .010 |
| 26.4 | 261.8 | 11.32 | .031 | 216.3 | 183.2 | 13.93 | .008 |
| 40.3 | 251.0 | 11.68 | .026 | 239.5 | 179.0 | 14.06 | .006 |
| 48.3 | 245.0 | 11.87 | .024 | 255.8 | 172.3 | 14.28 | .013 |
| 63.8 | 233.0 | 12.27 | .026 | 279.8 | 168.0 | 14.43 | .006 |
| 90.8 | 223.0 | 12.60 | .012 | | | | |

When 14.43 cc. had been taken up at 110°, the system was heated to 210°. In this process the sorption was found to have *decreased* to 10.82 cc. at 343 mm. pressure. In sixteen hours a further decrease to 10.13 cc. at 369 mm. occurred. On then returning to 110° resorption took place, giving 14.79 cc. at 157 mm., a value not greatly different from the original 14.43 cc. The pressure thereafter continued to fall slowly, and three hours later the sorption had risen to 15.00 cc.

The results with Cu I were very similar to those for Cu II, both as to rates and relative amounts adsorbed under different conditions. Since, however, the absolute quantities taken up were much smaller (again, as with hydrogen, by a factor of three or four), and since measurements were not made above 20°, the results for Cu I will not be detailed here.

**Nature of Sorption of Carbon Monoxide.**—From the relative sorption at different temperatures, and especially from the rate measurements, it is obvious that at least two different processes take place. At first glance it

might seem that the very rapid process is simply physical adsorption, and that the slow process, the rate of which increases with temperature, represents the activated adsorption. However, this view is at variance with the facts in several particulars. In the first place, the large adsorptions at low pressures obtained at −78.5 and 0° are indicative of activated adsorption. Second, the decrease in adsorption from −183 to −78.5 to 0° is far less than would be expected for purely physical adsorption. Carbon monoxide and nitrogen are closely alike in physical properties, and their physical adsorptions would be expected to vary with temperature in much the same way, yet comparison of Figs. 1 and 6 shows that the relative

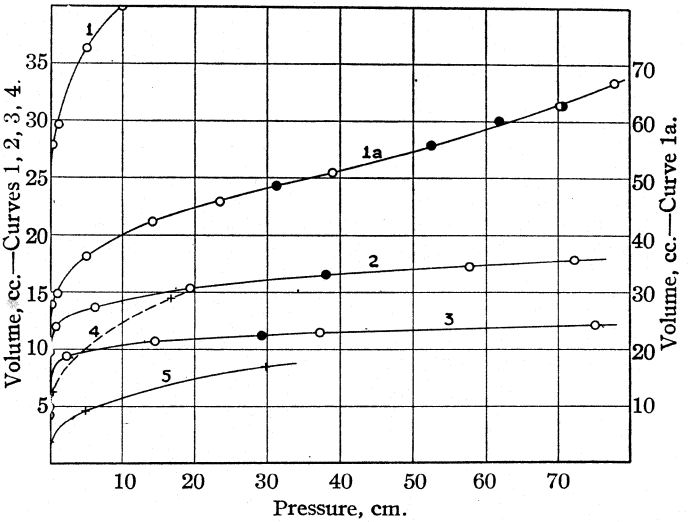


Fig. 6.—Isotherms for carbon monoxide: Curves 1 and 1a, −183°; Curve 2, −78.5°; Curve 3, 0°; Curve 4, final values at 110°; Curve 5, immediate adsorption at 110°.

adsorption of these two gases changes rapidly with increasing temperature. Thus the ratio of carbon monoxide to nitrogen adsorbed at 600 mm. is 1.54 at −183°, 8.7 at −78.5° and 110 at 0°; at 100 mm. the ratios for the same temperatures are 1.69, 38 and 410. Data in the literature for charcoal[13] and silica,[3] where the adsorptions are certainly of the physical type, give values for the $CO:N_2$ ratio which vary only between 1.2 and 1.8 in this range of temperature and pressure. A large part of the adsorption by Cu II at −78.5 and 0° must, therefore, be of the activated type, even though the gas was taken up with great rapidity. Finally, the data in Table IV show that after about 5 cc. had been taken up at 110°, the sorption of the next 1 cc. was very slow, whereas at 0 and −78.5° this sixth cc. was taken up practically instantaneously at very low pressures. Since

[13] Homfray, *Z. physik. Chem.*, **74**, 129 (1910).

the rate of a given type of adsorption cannot decrease with rising temperature, the slow process at 110° cannot represent either the physical or the activated adsorption. The evidence suggests that it is a process of solution, though an alternative possibility will be mentioned below.

While the data obtained do not permit a quantitative estimation of the separate amounts of gas taken up in each of the three ways, the situation seems to be qualitatively as follows. At −183° the major part of the adsorption is of the physical type, though the large adsorption at very low pressures, as compared with nitrogen, suggests that even at this temperature activated adsorption occurs. That the latter view is probably

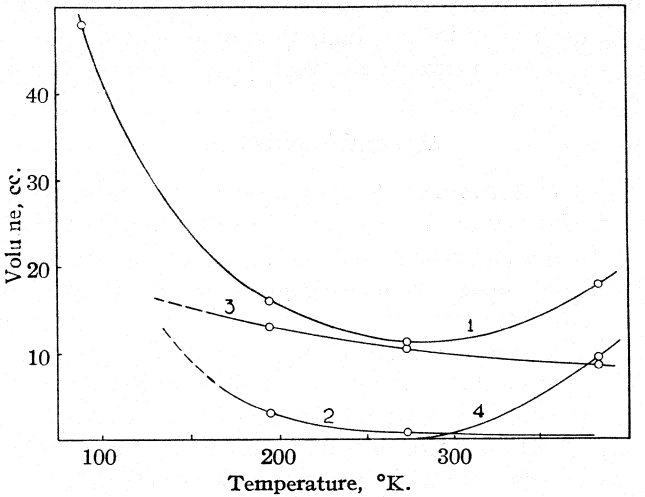


Fig. 7.—Isobars for carbon monoxide at 300 mm.: Curve 1, total sorption; Curve 2, physical adsorption; Curve 3, activated adsorption; Curve 4, solution.

correct is further indicated by the fact that at −78.5° the rate of activated adsorption of carbon monoxide is enormously greater than that of hydrogen; since at −183° there is a detectable activated adsorption of hydrogen, it would be expected that here carbon monoxide would be readily adsorbed in this form. At −78.5° the total adsorption of 16 cc. at 300 mm. consists of about 13 cc. of the activated type, and about 3 cc. of the physical type. At 0° the activated adsorption has decreased to about 10–11 cc., while the physical adsorption has fallen to less than 1 cc., and the process of solution has just begun to have an appreciable rate. At 110° and 300 mm. the physical type has become negligible, the activated type has decreased to about 8.5 cc. (Curve 5, Fig. 6), while the slow solution process accounts for about 9 cc., which is still short of equilibrium. This analysis is illustrated by the isobars for 300 mm. shown in Fig. 7, where Curve 2 represents the physical adsorption, Curve 3 the activated

adsorption, and Curve 4 shows the amount of solution which actually occurred though not of course the equilibrium value. Curve 1 represents the observed total sorption, and is the sum of Curves 2, 3 and 4.

It must be mentioned that there is no decisive evidence that the third process occurring is necessarily a process of solution. A second type of activated adsorption would be an alternative possibility. If this is the case, and if it can be shown that in this process the monoxide is adsorbed in such a way as to *decrease*, rather than increase, its chemical reactivity, a simple explanation would be thus provided for the well-known ineffectiveness of copper as a catalyst for many reactions involving carbon monoxide. However, since there is at present no convincing evidence for the occurrence in other systems of more than a single type of activated adsorption, it has seemed best to assume provisionally that we are dealing with a process of solution.

## General Discussion

**Physical versus Activated Adsorption.**—At low temperatures all three gases studied show typical physical adsorptions, and these are much greater for nitrogen and carbon monoxide than for hydrogen, as would be expected from the relative boiling points. With nitrogen no activated adsorption occurs within the range investigated, and accordingly increased temperature brings about a uniform decrease of adsorption to very small values. With hydrogen the rate of activated adsorption on the most active parts of the surface begins to be appreciable just above $-183°$. At $-78.5°$ a large fraction of the activated adsorption occurs rapidly, but the less active areas still give a slow rate, which is very much faster at $0°$. At these latter temperatures the physical adsorption has become practically negligible. In the case of carbon monoxide the rate of activated adsorption is very great even at $183°$, with the result that over a considerable range of temperature a pronounced overlapping of the two types of adsorption occurs. This last case is analogous to the situation observed in the earlier studies of the adsorption of the monoxide by oxide catalysts.[3]

**Thickness of Adsorbed Films.**—At first glance the points obtained for the adsorption of nitrogen and carbon monoxide at $-183°$ (Fig. 1, Curve 1a, Fig. 6, Curve 1a) appear to lie on fairly smooth curves. When the scale of these plots is taken into consideration, however, it will be realized that large deviations occasionally occur, amounting in some cases to more than 1 cc. In view of the great constancy of temperature and rapid rate of adsorption prevailing in these runs, the accidental errors of measurement are estimated not to exceed 0.05 cc. The irregularities, therefore, are apparently real. If the curves are drawn through the experimental points within the limit of error, a number of "breaks" appear. For nitrogen these occur at adsorptions of about 22 and 32 cc., for carbon

monoxide at about 30, 47 and possibly 60 cc. There may be other undetected breaks at smaller volumes.

The large intervals between breaks make it unlikely that this phenomenon is the same as the very small discontinuities previously referred to in connection with Fig. 2. The breaks here considered are believed to represent the volumes corresponding to the formation of successive adsorbed layers on the surface. If so, the adsorptions at $-183°$ and atmospheric pressure represent four or five molecular layers. This would certainly not be surprising in view of the fact that the temperature is only 12 and 7°, respectively, above the boiling points of nitrogen and carbon monoxide. Further discussion of this question will be reserved for a later paper in which the much more pronounced breaks observed with iron under similar conditions will be considered.

**Solubility.**—Fortunately there is little danger of confusing physical adsorption with solubility because in the cases so far studied the sorption due to the former process has become extremely small even at temperatures where the rate of solution is scarcely detectable. Our results show, however, that rate alone will not in general distinguish between activated adsorption and solution. Nevertheless, it is found that such a distinction is possible when all available data, including both rates and equilibria, are utilized. In this connection, experiments "with temperature variation," in the sense described above, furnish a most powerful tool, since under suitably chosen conditions they permit an approach to the two simultaneous equilibria from opposite sides.

The solubility of hydrogen in reduced copper at 0°, as observed in this investigation, is much greater than would be expected from an extrapolation of the solubilities obtained by Sieverts[8] for massive copper at temperatures above 400°. Previous experiments in this Laboratory by Griffin,[11] on the effect of small quantities of carbon monoxide on the sorption of hydrogen by copper at 0 and 20°, lead to the same conclusion. The recent results of Ward[7] seem also to point in the same direction, although the solubilities he has reported may be too high, particularly at the lower temperatures, because of his disregard of activated adsorption. While these results at lower temperatures are not necessarily in conflict with Sieverts' data, Ward has advanced the suggestive idea that the low-temperature solubilities represent intergranular penetration rather than actual solubility in the crystal lattice.

## Summary

1. The sorptions of nitrogen, hydrogen and carbon monoxide by two samples of reduced copper have been measured at pressures to one atmosphere and at temperatures down to 78°K.

2. It is shown that in general three definitely distinguishable processes

occur, (a) surface adsorption of the physical type, (b) surface adsorption of the activated type, and (c) solubility. Under certain conditions one process may predominate, while under other conditions two or more of these phenomena may occur simultaneously, so that the total observed sorption is the sum of the amounts taken up in the several ways.

3. Within the range investigated, nitrogen shows only physical adsorption, characterized by a rapid rate and a small heat of adsorption.

4. Hydrogen exhibits all three processes. At the lowest temperatures only physical adsorption occurs, at $-78.5°$ activated adsorption is the predominating process, while at $0°$ both activated adsorption and solution occur. The amounts of hydrogen taken up in each of the three ways have been determined.

5. In the case of carbon monoxide three different processes also are found. Two of these are shown to be physical and activated adsorption, while the third is either solubility or a second kind of activated adsorption.

UNIVERSITY, VIRGINIA

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

# AN APPARATUS FOR MEASURING PARTIAL VAPOR PRESSURES OF BINARY LIQUID SYSTEMS

BY O. A. NELSON

RECEIVED DECEMBER 3, 1931 PUBLISHED APRIL 6, 1932

One of the commonest methods used in the determination of partial vapor pressure of binary mixtures is the so-called dynamic method. This method consists essentially in distilling off a small portion from a large volume of mixture, and then analyzing the distillate obtained. That this method is open to rather serious objections is admitted by many investigators. Zawidski[1] has pointed out that the volume of the mixture used is often too small, and as a result the composition and boiling point vary too much during the distillation. Kuenen[2] stated that the temperature of the vapor varied considerably, and that there was often an appreciable difference in temperature between the liquid mixture and the vapor, due probably to superheating of the liquid or cooling of the vapors. Another drawback to this method according to Rosanoff and co-workers[3] is the fact that only relatively small quantities of the distillate are available for analysis. Other methods might be discussed, but the reader is referred to the article by Rosanoff[3] for more complete criticisms of methods available.

[1] Zawidski, *Z. physik. Chem.*, **35**, 129 (1901).

[2] Kuenen, "Verdampfung und Verflüssigung von Gemischen," Leipzig, 1906.

[3] Rosanoff and co-workers, THIS JOURNAL, **31**, 451 (1909).

**Discussion of Method.**—Rosanoff and co-workers[3] added gradually to the distilling mixture during distillation such quantities of the lower boiling component as would keep the distillation temperature constant. Also to make certain that equilibrium between liquid and vapor was established they passed the vapors through an equilibrium chamber containing a liquid mixture of the same components as the distilling mixture. They state in this connection, "True equilibrium can only be attained and its attainment demonstrated by passing the vapor of a composition obtained by one or another method through a liquid mixture of the same components." Rosanoff's method, while a decided improvement over the older methods, suffers from the weakness that it is very difficult to add the lower boiling component at such a rate as to maintain a mixture of constant composition in the boiling chamber. This method was tried by Young and Nelson[4] in their work on the binary mixture carbon tetrachloride–ethylene dichloride, but it was found to be almost impossible to prevent changes in composition in the boiling mixture. Very satisfactory results were obtained by a combination of the methods of Rosanoff and of Carveth[5] the latter of whom, instead of adding one pure component, added a mixture of approximately the same composition as the distillate and obtained good results. The method was carried out in two steps. In the first the pure components were added alternately and in small increments to maintain an approximately constant boiling temperature, and in the second the distillate obtained during the first step was added to the boiling mixture at as nearly as possible the same rate as distillation proceeded. The boiling point of the mixture during this step could be kept within $\pm 0.01°$ indicating very constant composition.

In the apparatus shown in Fig. 1[6] the two-step method has been done away with, although the principles involved have not been changed. In this apparatus, designed toward the end of the work referred to,[4] the process is made automatic by adding to the apparatus a tube through which liquid flows back from the receiver to the boiler exactly as fast as other liquid distils into the receiver. The distillation is continued until the temperature of the distilling liquid becomes constant over a long period of time. The equilibrium chamber suggested by Rosanoff is retained as a further assurance that equilibrium is reached. The apparatus is made of Pyrex glass and in one piece, all points being sealed to prevent leaks of vapors or liquids. The dimensions of the different parts are as follows. The boiler was made from a 250-cc. round-bottomed flask and the receiver from a 200-cc. flask. The chamber containing the thermometer well is about 12.7 cm. long and 2.5 cm. in diameter, and the thermometer well itself is just large enough to accommodate the end of a Beckmann thermometer. Some mercury is poured into the thermometer well in order to make better contact between the hot liquid mixture and the thermometer. The equilibrium chamber is

[4] Young and Nelson, *Ind. Eng. Chem., Anal. Ed.*, **4**, 67 (1932).

[5] Rosanoff and Carveth, *J. Phys. Chem.*, **3**, 193 (1899).

[6] The author is indebted to Mr. R. M. Baker of the Division of Chemical Engineering for preparing the drawing of this apparatus.

also about 12.7 by 2.5 cm. and is surrounded by a jacket 14 cm. long by 5 cm. in diameter. The condenser is 23 cm. long, and the return tube from the receiving flask is placed in such a position that about 150 cc. of the distillate is made available for analysis. The return tube obviously must slope downward from the receiver to the filling tube to facilitate the return of distillate. The reflux condensers are ordinary 20–25 cm. stock condensers.

The operation of the apparatus is almost self-evident. Briefly, however, it is as follows. The boiler and receiver of the apparatus are filled either with the same liquid mixture, or the receiver may be filled with a mixture somewhat richer in the lower boiling components. The boiler is heated electrically. During operation the mixture in the boiler spurts against the thermometer well, and also against the equilibrium chamber. The slightest change in composition of the mixture is readily detected by the temperature change, as shown by means of a Beckmann thermometer. Vapors from the liquid thrown against the thermometer well pass into the equilibrium chamber, where a portion condenses to form a liquid for the vapors to bubble through. The top part of the equilibrium chamber is then gently heated by means of an electric heater, to prevent refluxing of the escaping vapors. When the proper amount of heat is supplied, the level of the liquid in the equilibrium chamber remains constant. With high boiling mixtures the equilibrium chamber should be insulated with a layer of asbestos or other suitable insulating material. As the boiling is continued the vapors are condensed and caught in the receiver for the distillate. This receiver, of about 200 cc. capacity, is fitted with a return tube, which carries the distillate back to the boiler. If now the returning distillate does not have the same composition as the mixture in the boiler, the composition will gradually change, as will be observed from the change in boiling point. The process must obviously be continued until no change in temperature can be detected. The composition of both liquids may then be determined either chemically or by physical means depending on the components.

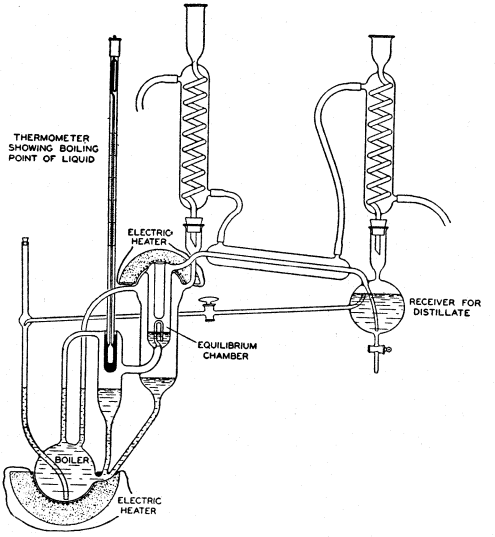


Fig. 1.—Apparatus for measuring partial vapor pressures of binary mixtures.

The total pressure being known, in most cases the partial pressures of the components are readily calculated from the ratio of the components, expressed in moles.

It is evident that for very accurate work the changes in atmospheric pressures must be allowed for. If such variations of pressure become appreciable, a monostat should be constructed and attached. This device may be connected to the upper end of the reflux condensers.

This apparatus was used toward the end of the work on ethylene dichloride–carbon tetrachloride mixtures, and all points previously obtained were checked. The values obtained by this apparatus agreed perfectly

with those obtained by the method described previously. It is felt that the use of this apparatus offers a rapid as well as a very accurate means for determining partial vapor pressures of binary mixtures.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# THE ELECTRON AFFINITY OF FREE RADICALS. III. FURTHER STUDIES OF FREE RADICALS CONTAINING BIPHENYL AND NAPHTHYL GROUPS

BY HENRY E. BENT AND MAURICE DORFMAN

RECEIVED DECEMBER 4, 1931 PUBLISHED APRIL 6, 1932

The addition of an alkali metal to an unsaturated compound is a type of reaction which is peculiarly adapted for study in connection with the problem of finding the effect on the strength of a given bond of various substitutions in a molecule. Heats of combustion and dissociation constants of acids give similar data but have their own peculiar limitations. Heats of combustion are commonly so large as to mask very largely changes in a single bond. Ionization data for acids are difficult to obtain in solvents which have a stronger affinity for the proton than the base from which the acid is derived. The addition of alkali metals to unsaturated compounds supplies a very wide range of reactions to be studied and reactions which are at least in some cases reversible.

Not only will sodium add to such unsaturated single bond compounds as organic free radicals but it will also add to some double bond compounds such as ketones and olefinic compounds and to apparently saturated molecules such as triphenyl boron and triphenyl aluminum. The variety of reactions which may be studied is, therefore, all that can be desired providing equilibrium measurements are possible. It has been shown[1] that the sodium may be removed from the free radical addition compounds with the aid of mercury and that by knowing the concentration of the amalgam which is in equilibrium with the free radical and the addition compound, the free energy for the addition of sodium to the free radical may be calculated (Equation 2). A comparison of various free radicals, since in every case sodium ion is formed, is, therefore, a comparison of the reaction

$$\mathrm{Ar{:}\ddot{C}.} + \ominus = \mathrm{Ar{:}\ddot{C}:} \qquad (1)$$

of formation of the negative ion from the free radical (Equation 1). The equilibrium studied experimentally is

$$\mathrm{Na + R = Na^+ + R^-} \qquad (2)$$

[1] H. E. Bent, THIS JOURNAL, **52**, 1498 (1930).

In these equations Ar represents any aromatic group while R represents the whole free radical, such as triphenylmethyl.

It has been found that the free energy changes for reaction (2) and, therefore, also for reaction (1) in the case of four free radicals, do not differ by more than 2 kg. cal. Therefore, the addition of an electron to an "odd" molecule to complete the group of eight electrons about the central carbon, or in other words the addition of an electron to an unshared electron to form an electron pair involves an energy change which is practically independent of the substituents on the atom involved. This fact is of particular interest inasmuch as a pair of similar electrons forms the non-polar bond in the corresponding ethanes. That the energy here measured should be the same for a variety of compounds is additional evidence that the electron pair, as first suggested by G. N. Lewis, acts as a unit in the formation of non-polar bonds.

A close examination of the data reported in the second paper of this series[2] brought out the fact that the variations in the electron affinity which are less than 2 kg. cal. are quite regular, larger molecules having the stronger affinity. This observation coupled with the observation that it is the larger of these free radicals which shows the smallest tendency to associate forming the ethane led to the hypothesis that the weakness of the bond which leads to the formation of the ethane is due not to the force between two carbons being less but to the fact that the force has operated through a smaller distance, due to the steric hindrance of the large phenyl groups, and, therefore, the resulting energy of binding is much less.

These deductions have been based on the study of but four compounds. This number being so small, it would seem very desirable to study a larger number of compounds of the same type in order to verify or delimit these tentative conclusions. This paper describes work on four more compounds which may be described as triphenylmethyl in which biphenyl or naphthyl has replaced one or more phenyl groups. These compounds are all of the same type as those heretofore studied in that they contain only aromatic hydrocarbon substituents. The results are entirely in accord with those previously reported. The ease of removing sodium from the addition compound is about the same for all of the compounds studied, the larger free radicals having a slightly greater affinity for the sodium, and, therefore, a slightly greater electron affinity. The effect of the various groups is nearly additive, so that it is possible to predict with considerable accuracy a value for the equilibrium constant of the reaction.

## Procedure

The experimental procedure has been modified somewhat with the result that the data are considerably more accurate. The method of making the amalgams and intro-

[2] H. E. Bent, THIS JOURNAL, 53, 1786 (1931).

ducing them into the evacuated system has been developed to a point where it now seems quite satisfactory and not very laborious. Figure 1 shows the flask used in preparing the amalgams. Sodium is first dried from oil with filter paper, surface oxide removed as shavings, and introduced into the straight tube above the flask. A glass weight above the sodium helps to break the oxide shell, which otherwise retards the flow of liquid metal. The tube is then sealed off as shown and the whole system evacuated. With the mercury pump still in operation the sodium is gently warmed. This gives time for reaction of the metal with any hydroxide which may have been formed during the brief time required for sealing the tube. Finally, the temperature is raised to the melting point, the molten sodium running through the constriction and giving a perfectly clean surface. Mercury is then distilled from the small flask with the aid of a small flame from a Bunsen burner. The apparatus is evacuated during the whole distillation, which may be carried out in a few hours with practically no supervision. Early in the process, after about three equivalents of mercury have been added, the amalgam is heated to the melting point in order to insure complete solution of the rather infusible compounds. Thereafter the latent heat of condensation maintains the temperature above the melting point of the amalgam. When it is estimated that the composition is near that of the saturated amalgam, about five atom per cent., the flask is allowed to cool to room temperature. If the amount of solid phase is too large, further mercury may be introduced into the small flask through the stopcock and the distillation continued until there is but a small amount of solid phase. The flask is then sealed to another flask by means of the three way stopcock, this latter flask evacuated, the pump sealed off and then by tipping the saturated amalgam is poured into the second flask. Slight warming before pouring ensures an amalgam which will be saturated when cooled.

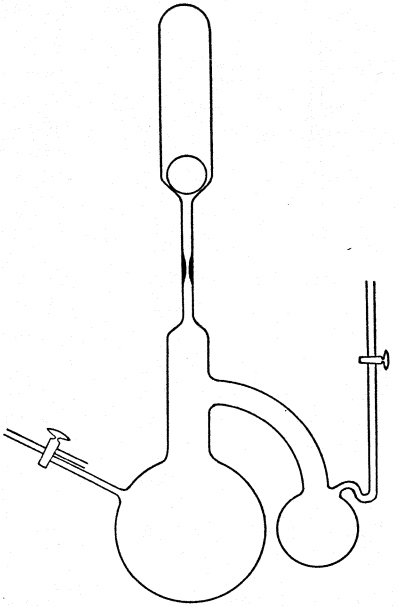

Fig. 1.—Apparatus for preparing amalgam.

The flask containing the saturated amalgam is then inverted, the stopcock passing through a ring padded with cloth, and sealed to a second stopcock, Fig. 2. This has been found to be necessary due to the fact that prolonged contact of amalgam with stopcock grease gradually spoils the grease in a band around the plug passing over the two ends of the bore. The upper stopcock, therefore, serves merely to hold the amalgam, the lower one serving to hold the vacuum. The lower one is, of course, opened before any amalgam is taken from the flask. The ether is kept in the lower flask, stored over sodium–potassium alloy as described in the first paper of this series. It has been found possible to keep the stopcock of this flask in good condition by maintaining it a few degrees above room temperature. After perhaps twenty to thirty samples have been removed, it sometimes becomes necessary to regrease this cock. This may be done without admitting air to the flask by first warming the flask with a beaker of water to a temperature five to ten degrees above the boiling point of ether. The plug is then removed, and old grease is wiped clean while ether is slowly distilling out of the flask. Before regreasing, the plug is heated considerably above the temperature of the bath by im-

mersing it in a beaker of boiling carbon tetrachloride. On inserting the hot regreased plug very little ether condenses in the grease. The flask is then rapidly cooled by ice water before the plug has time to cool below the temperature of the ether. The tube surrounding the lead to the apparatus is filled with ice and water when it is desired to introduce ether, the mercury pump being cut off by the cock in the pump line.

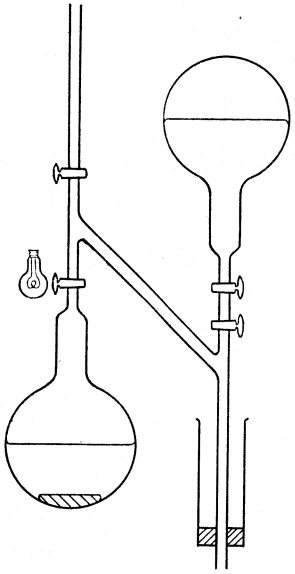

Fig. 2.—Storage flasks for ether and amalgam.

Two changes in manipulation have been made which considerably improve the reliability of the data. Heretofore it has always been noticed that a small amount of liquid is decolorized when filtered and transferred to the second tube of the apparatus[3] for treatment with mercury. The amount has been so small, about 5%, as not to affect the results seriously, but has been a continued source of uncertainty. This has been practically eliminated by freezing the ether solution in liquid air before sealing off from the pump line or sealing between the two tubes. Apparently there is sufficient decomposition of ether at the temperature of Pyrex glass during the sealing to liberate an appreciable amount of water. A second improvement in technique has been to rinse the apparatus with ether vapor before introducing the bulk of the ether. It is not possible to bake out the Pyrex thoroughly before each run due to the fact that the sample of chloride is placed in the tube before attaching to the pump for evacuation. The small amount of oxygen or water which is so tenaciously held by the glass can apparently be removed by displacing it with ether. The procedure is to admit a little ether to the apparatus after a preliminary evacuation, and then to pump down again to about $10^{-4}$ mm. of mercury pressure. Presumably the ether is adsorbed on the glass more strongly than the water, and, therefore, cleans up the surface. It may be that Ziegler's[4] success in cleaning up the glass in his experiments on hexaphenylethane in very dilute solution was due rather to the solvent used than to the free radical dissolved in it.

## Materials

The authors are greatly indebted to Dr. W. F. Bruce, who prepared the carbinols from which our free radicals were derived. In every case the carbinol was converted into the corresponding chloride with the aid of hydrogen chloride gas. Inasmuch as some difficulties were encountered in the preparation some detail as to the procedure will be given. The most difficult part of the problem seemed to be to obtain the chlorides of such purity that a Carius analysis would give at least 97% of the calculated amount of chlorine. Since the chief impurity was carbinol, formed by hydrolysis, this gave an excellent check on the purity of the compound. In some cases there were highly colored impurities which crystallized separately from the chloride but had solubilities so nearly the same as the chloride as to make separation difficult.

[3] Tube A, Fig. 1, Reference 1.

[4] Ziegler and Ewald, *Ann.*, **473**, 183 (1919).

**β-Naphthyldiphenylchloromethane.**—The carbinol was prepared according to the directions in the literature,[5] dissolved in ethyl ether and converted into the chloride by treating with dry hydrogen chloride gas. In order to avoid the difficulties with tarry impurities reported by Gomberg and Sullivan, which required treatment with bone black and recrystallization, we tried using freshly distilled ether, hoping that the absence of peroxide would give a cleaner product. This proved to be the case, fine white crystals being obtained without the necessity of using bone black. It is especially desirable to avoid the use of bone black on account of the hydrolysis of the chloride which is certain to take place unless great precautions are taken to have the bone black free from adsorbed moisture. The chloride was recrystallized three times by adding petroleum ether to the ethyl ether solution and cooling to 0°. The final product melted at 95°. The previously reported melting point is 94.5°.

*Anal.* Calcd. for $C_{23}H_{17}Cl$: Cl, 10.79. Found: Cl, 10.73, 10.75.

**Phenyldibiphenylchloromethane.**—The carbinol was prepared according to the directions of Schlenk.[6] Considerable difficulty was encountered, however, in attempting to obtain the carbinol from the benzene solution in which it was prepared, only tars or oils being obtained. The attempt was then made to treat the benzene solution with hydrogen chloride and crystallize the chloride. Here also the attempts to crystallize the chloride from benzene, ether, petroleum ether, ligroin and various mixtures of these resulted in nothing but oils. The treatment with hydrogen chloride produced an intense red color and a small amount of red crystalline material separated but apparently none of the desired chloride. The difficulties encountered were undoubtedly due to the fact that the carbinol was too impure to start with. However, attempts to purify the solution by treating it with bone black, or by steam distillation of the oily carbinol obtained by precipitation, while undoubtedly removing some impurities, did not suffice to give crystalline material. Finally it was found that fractional precipitation of tarry materials by means of petroleum ether, gave material which became continually lighter in color and more crystalline until the last half was almost white; 5 g. of this material was dissolved in 75 cc. of benzene. Treatment with calcium chloride and dry hydrogen chloride again gave a bright red solution and on adding 50 cc. of petroleum ether and cooling to 0°, about 0.4 g. of red crystals formed, leaving the mother liquor much lighter in color. The liquid was decanted from these crystals, evaporated to 20 cc., 30 cc. of petroleum ether added and the solution again allowed to stand at 0°. Crystals with but a slight pink tinge formed from this solution; these were crystallized four times more from benzene and petroleum ether. The final product weighed 1.4 g. and melted at 132°. The melting point previously reported is 131.5°.

*Anal.* Calcd. for $C_{30}H_{25}Cl$: Cl, 8.25. Found: Cl, 8.01, 8.24.

**α-Naphthyldibiphenylchloromethane.**—The carbinol prepared by the method of Schlenk and Bornhardt[7] and recrystallized from xylene melted from 211–214°, while their material melted at 228°. We, therefore, extracted the carbinol from excess dibiphenyl ketone with ether, using a continuous extraction apparatus, and thereby obtained material melting from 225–227°. Six grams of this material was then dissolved in 175 cc. of benzene, calcium chloride added and the solution treated with hydrogen chloride. A small amount of white solid precipitated and was discarded, while the solution became intensely blue in color. This color was largely removed by treatment with bone black, leaving a light orange colored liquid. The bone black was carefully dried before use in order to prevent hydrolysis of the chloride, by evaporating to dryness three

[5] Gomberg and Sullivan, THIS JOURNAL, **44**, 1813 (1922).

[6] Schlenk, *Ann.*, **368**, 300 (1909).

[7] Schlenk and Bornhardt, *Ber.*, **46**, 1482 (1913).

times from benzene and finally heating to red heat and cooling in a desiccator; 175 cc. of petroleum ether was added to the benzene solution of the chloride and the solution cooled to 0°. About 0.5 g. of a blue solid separated and was discarded. The mother liquor was evaporated to 50 cc., 50 cc. of petroleum ether added and the solution allowed to stand at room temperature. A white solid with orange crystals separated. Recrystallization twice from benzene and petroleum ether gave a final product which weighed one gram, was composed of small white needles and melted at 215–216°. The melting point previously reported is 214–216°.

*Anal.* Calcd. for $C_{35}H_{25}Cl$: Cl, 7.38. Found: Cl, 7.14, 7.20.

**Tribiphenylchloromethane.**—The procedure for preparing this compound differed somewhat from that described in the literature.[8] Two grams of magnesium powder activated by Baeyer's method[9] was added in three nearly equal portions to a solution of 15 g. of dry *p*-bromobiphenyl[10] in 25 cc. of dry ether. A vigorous reaction took place. After the solution had been refluxed for three hours, 25 cc. of benzene was added and 15 g. of dibiphenyl ketone in four portions. The solution of the ketone occurred rapidly with evolution of considerable heat and the production of a green color which later became purple. The material was refluxed for four hours and the magnesium derivative then obtained in solid form by the addition of petroleum ether. This material was rubbed with ammonium chloride solution in a mortar and recrystallized from benzene. The melting point of the product was 196–199°. After extraction with ethyl ether to separate the product from any unchanged ketone the melting point was 205–207°. The previously recorded value is 208°. Five grams of this carbinol was treated with dry hydrogen chloride gas in the presence of a little calcium chloride. The solution became dark purple in color and retained this color after boiling down to 50 cc. After standing at room temperature a solid precipitated, leaving the mother liquor yellow in color. After decantation an equal volume of petroleum ether was added and the solution allowed to stand at 0°. Small white crystals formed together with a small amount of an intensely colored purple solid. Upon warming with benzene, however, the white crystals dissolved first so that it was possible to obtain a separation by rapid decantation at the proper point. Three more crystallizations from benzene and petroleum ether gave one gram of white material melting at 198°. The recorded value in the literature is 195°.

*Anal.* Calcd. for $C_{37}H_{27}Cl$: Cl, 7.00. Found: Cl, 6.84, 6.80.

## Experimental Results

Table I gives the experimental data for the equilibrium measurements. These were obtained over as large a range of concentration as the solubility of the compounds and the analytical procedure would permit. The three columns headed log $K_2$ give values of the equilibrium constant for equation (2). The column headed $K_3 = \infty$ is included in order to show the magnitude of the change in the equilibrium constant which would be produced by assuming complete dissociation of the sodium addition compound into sodium ion and a free radical ion with one negative charge. These compounds undoubtedly are not completely dissociated and, therefore, a value

[8] Schlenk and Weickel, *Ann.*, **372**, 1 (1910); Schmidlin, *Ber.*, **45**, 171 (1912); Schlenk, *ibid.*, **46**, 1475 (1913); Schmidlin, "Das Triphenylmethyl," p. 169.

[9] Houben–Weyl, Vol. IV, 1924, 724.

[10] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 42.

for this dissociation constant of $10^{-4}$ has been assumed for all of these compounds.[1] A variation of one power of ten in this constant changes the value of log $K_2$ by about 0.5. A second dissociation which must be considered is that of the ethane into the free radical. The particular compounds chosen for this study were selected on account of the fact that the ethanes are so nearly completely dissociated into the free radicals at the concentrations at which we are working that we may assume complete dissociation. In the case of the last compound in the table, however, this assumption is not justified. The value for the dissociation constant for this ethane has been taken as $10^{-3}$, based on the fact that molecular weight determinations in naphthalene indicate this compound to have a constant ten times as large as hexaphenylethane.[11] The value for hexaphenylethane used in the first paper of this series was $10^{-4}$. All values for these constants are here calculated with concentrations expressed as mole fractions. Since all of the other free radicals have been shown by molecular weight determinations to be more dissociated than β-naphthyldiphenylmethyl, it is legitimate to assume complete dissociation in the calculations.

The relation between the total amount of compound in solution and the amount which is dissociated may be derived in the following manner: let $R$ be the number of moles of free radical, $R_2$ the number of moles of ethane, $n$ the number of moles of solvent, $K$ the equilibrium constant for the reaction

$$R_2 = 2R$$

and $a$ be the amount of free radical determined analytically (that is, $R + 2R_2$). We then have the equations

$$a = R + 2R_2$$
$$K = \frac{(R/n)^2}{R_2/n} = \frac{R^2}{nR_2}$$

Eliminating $R_2$ gives a quadratic equation in $R$

$$R = \frac{-1 + \sqrt{1 + 8a/nK}}{4/nK}$$

only the positive value of the root being significant. This may be expanded by the binomial theorem giving

$$R = a - 2a^2/nK + 8a^3/n^2K^2 \ldots$$

Therefore

$$R/a = \alpha = 1 - 2a/nK + 8a^2/n^2K^2 \ldots$$

when $\alpha$ is fraction dissociated. Hence when $a = {}^1/_{10}nK$, the error in assuming complete dissociation is less than 15%, and if $K$ is larger by a factor of 10, the error is about 2%.

Making use of the relation $\Delta F = -RT \ln K$ we may convert these values

[11] P. Walden, "Chemie der freien Radikale," S. Hirzel, Leipzig, 1924.

of the equilibrium constants into free energy values as shown in the last column of the table.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE ADDITION OF SODIUM TO FREE RADICALS

| Compound | G. atoms of Na removed $\times 10^4$ | G. atoms of Na left $\times 10^4$ | Moles of ether | G. atoms of mercury | Log $K_2$ $K_3 = \infty$ | Log $K_2$ $K_3 = 10^{-4}$ | Mean | $-\Delta F$ |
|---|---|---|---|---|---|---|---|---|
| Phenyldibi- | 0.125 | 0.407 | 0.152 | 3.92 | 15.33 | 14.54 | | |
| phenyl- | .150 | .586 | .162 | 4.87 | 15.55 | 14.76 | | |
| methyl | .201 | .932 | .181 | 2.57 | 15.37 | 14.47 | | |
| | .487 | 1.673 | .151 | 4.72 | 15.46 | 14.28 | | |
| | .627 | 2.983 | .165 | 4.80 | 15.61 | 14.35 | 14.48 | 19.8 |
| Tribiphenyl- | .085 | 0.785 | .151 | 3.96 | 16.24 | 15.33 | | |
| methyl | .118 | .614 | .144 | 4.77 | 15.84 | 15.00 | | |
| | .198 | 1.217 | .139 | 4.97 | 16.02 | 14.93 | | |
| | .211 | 1.709 | .142 | 5.05 | 16.26 | 15.05 | | |
| | .266 | 1.994 | .182 | 5.01 | 16.08 | 14.90 | 15.04 | 20.6 |
| $\alpha$-Naphthyl- | .0081 | 0.245 | .158 | 4.81 | 15.34 | 14.81 | | |
| dibiphenyl- | .0225 | 1.075 | .190 | 4.92 | 15.66 | 14.73 | | |
| methyl | .105 | 0.378 | .165 | 4.92 | 15.48 | 14.83 | | |
| | .211 | .835 | .171 | 5.55 | 15.60 | 14.71 | | |
| | .307 | 1.969 | .181 | 4.71 | 15.92 | 14.75 | 14.77 | 20.2 |
| $\beta$-Naphthyl- | .246 | 0.466 | .121 | 2.81 | | 14.14 | | |
| diphenyl- | .269 | .443 | .164 | 3.22 | | 14.03 | | |
| methyl | .718 | 1.081 | .156 | 2.96 | | 13.72 | | |
| | 1.307 | 1.079 | .105 | 3.27 | | 13.55 | | |
| | 1.526 | 1.557 | .138 | 3.31 | | 13.44 | 13.78 | 18.6 |

These values are for the reaction of addition of sodium to free radical to form the positive sodium ion and the negative free radical ion. The standard state for the sodium is taken as the metal and for the other materials the activity is taken as equal to the mole fraction.

These free energy values together with those previously obtained have been expressed graphically in Fig. 3, in which the free energy is plotted as ordinate and the number of benzene rings in the molecule as the abscissa. The upper curve is the biphenyl series, starting with triphenylmethyl and passing to the compounds which contain one, two and three biphenyl groups. The lower curve has also been drawn through the point for triphenylmethyl and might be called the naphthyl curve, since there is one naphthyl group in the rest of the compounds. The point on this curve at 18.6 kg. cal. represents both $\alpha$-naphthyldiphenylmethyl and $\beta$-naphthyldiphenylmethyl, both of these compounds giving the same value. The last two compounds contain one and two biphenyl groups, respectively, in addition to the $\alpha$-naphthyl group. These curves substantiate the conclusions of the previous paper of this series. In the first place the values of the free energy change for the reactions all fall within the rather narrow range of 2.5 kg. cal. In the second place, the effect of replacing phenyl by

naphthyl or biphenyl is nearly additive, the former apparently having a slightly smaller effect than the latter. It would seem probable that a prediction could be made for trinaphthylmethyl of 19.3 ± 0.3.

It is possible from these data to infer something as to the dissociation constant of the sodium addition compounds. Since there are almost no experimental data on the subject, a value of $10^{-4}$ has been assumed for all of these compounds.[1] The fact that this assumption gives values of $\Delta F$ which differ little from each other, indicates that the assumption is probably correct. It is possible that the dissociation constant changes as we pass from one compound to another, and that these changes are just compensated by some other factor changing in the opposite direction. Since such an assumption is less probable, we may infer that the dissociation constants for these sodium addition compounds are essentially the same. It should be noted, however, that $\Delta F$ is not particularly sensitive to changes in the dissociation constant and, therefore, these data indicate only that this constant does not change by many powers of ten.

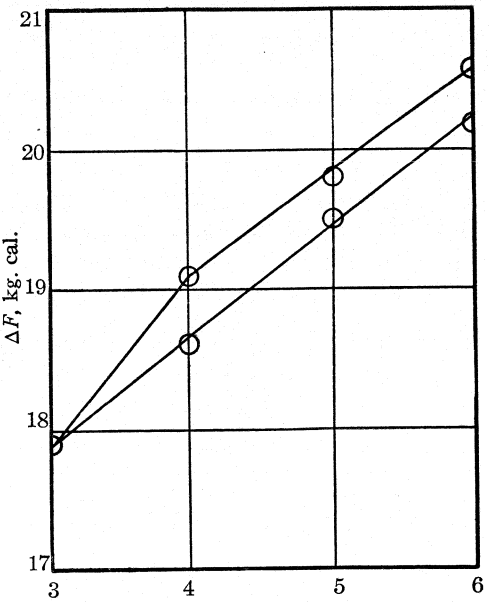


Fig. 3.—The free energy of addition of sodium to free radicals. The upper curve is for the biphenyl series. The compounds represented by the lower curve may be considered as triphenylmethyl in which the first phenyl is replaced by naphthyl and the second and third by biphenyl.

## Conclusions

The reaction of addition of sodium to four organic free radicals has been studied quantitatively, these compounds being phenyldibiphenylmethyl, tribiphenylmethyl, α-naphthyldibiphenylmethyl, and β-naphthyldiphenylmethyl.

The conclusions of the second paper of this series have been found to be borne out by this study. These conclusions were, first, that the values for the free energy of addition of sodium to these free radicals all fall within rather narrow limits; second, that within these limits the effects produced by the various groups are additive.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 17]

# A COMPLEX CYANIDE OF TRIVALENT MOLYBDENUM

BY RALPH C. YOUNG

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Although complex chlorides, bromides and thiocyanates of trivalent molybdenum are known, previous attempts to produce a trivalent complex cyanide have resulted in the formation of the octacyanide of tetravalent molybdenum, and it has been the practice to consider the oxidation of the molybdenum as due to the oxygen of the air and to express the result by equations similar to the following

$$4K_3MoCl_6 + 32KCN + 2H_2O + O_2 = 4K_4Mo(CN)_8 + 24KCl + 4KOH$$

as was done by Bucknall and Wardlaw.[1] In the case of the thiocyanate, however, replacement occurs without oxidation

$$K_3MoCl_6 + 6KSCN = K_3Mo(SCN)_6 + 6KCl$$

The problem of ascertaining why oxidation should take place in the case of the cyanide and not in that of the thiocyanate was undertaken with a view to applying the facts found to the prevention of this oxidation and the preparation of a trivalent complex cyanide.

The oxidation of the molybdenum to the tetravalent condition, it was found, could not be prevented when the reaction between potassium molybdenum hexachloride, $K_3MoCl_6$, prepared by the method of Bucknall, Carter and Wardlaw,[2] and potassium cyanide was carried out at approximately 90° in oxygen-free water and in an atmosphere of nitrogen, nor when the reaction was allowed to take place at the above temperature in a previously evacuated apparatus.

When potassium molybdenum hexachloride was heated with potassium hydroxide solution in the absence of air, the precipitated black sesquioxide was found to react with the water to evolve hydrogen, the molybdenum being oxidized to a higher valence state. It is known that the sesquioxide is oxidized in the air to the brown dioxide. Since potassium cyanide solution was found to react in presence of air with the sesquioxide and also with the dioxide to produce the octacyanide, it would seem possible that the following series of changes could take place at elevated temperatures in the absence of oxygen, in the reaction between the complex hexachloride and potassium cyanide solution.

$$CN^- + H_2O \rightleftharpoons OH^- + HCN$$
$$MoCl_6^{\equiv} = 3OH^- = Mo(OH)_3 + 6Cl^-$$
$$H_2O + Mo(OH)_3 + 8CN^- = Mo(CN)_8^{\equiv\equiv} + 4OH^- + (H)$$

[1] Bucknall and Wardlaw, *J. Chem. Soc.*, 2988 (1927).

[2] Bucknall, Carter and Wardlaw, *ibid.*, 512 (1927).

One noted the dark red solution, the color of which is due to the $MoCl_6^{=}$ ion, change to a black opaque colloidal solution and finally to a transparent orange-yellow due to the $Mo(CN)_8^{====}$ ion. The black colloidal material is probably molybdenum trihydroxide, as one obtains the same result when the hexachloride is first treated with alkali. No hydrogen is evolved in the reaction of potassium molybdenum hexachloride with potassium cyanide, although it was formed with potassium hydroxide. The fact that hydrogen is not evolved may be accounted for on the assumption that it is consumed by interaction with hydrocyanic acid, which is known to be reduced by metals in acid solution to methylamine and in neutral solution to formaldehyde and ammonia.

**The Preparation of Tripotassium Molybdenum Heptacyanide Dihydrate.**—By allowing the reaction between potassium molybdenum hexachloride and potassium cyanide to take place at room temperature, in oxygen-free water, and in an atmosphere of nitrogen, there was obtained a black, crystalline compound of trivalent molybdenum, analyses of which correspond to the formula, $K_4Mo(CN)_7.2H_2O$, or $K_4\left[Mo\begin{matrix}(CN)_7\\H_2O\end{matrix}\right]\cdot H_2O$. The method of preparation follows.

Seven grams of the hexachloride and 12 g. of potassium cyanide were introduced into the reaction vessel at C, Fig. 1, while nitrogen was allowed to enter at A. Tube C was sealed near the end, the nitrogen escaping now at B. After all the air was displaced with nitrogen, 70 cc. of water saturated with nitrogen was allowed to enter at B by opening D, A being closed. Stopcocks D and B were now closed and the tube with contents was shaken until complete solution had taken place. The red transparent solution gradually assumed an opaque, black and colloidal appearance and finally at the end of eighteen hours was again transparent and of a red-brown color. Thirty cc. of alcohol saturated with nitrogen was allowed to enter the reaction vessel through tube B, and was thoroughly mixed with the contents. No precipitation took place but on cooling the vessel in ice water black crystals were deposited in the form of flat plates. They fell to the bottom of the container and after crystallization was complete, the supernatant liquid was allowed to run out at A while nitrogen passed in at B. The crystals were washed several times with 80% alcohol, saturated with nitrogen, and finally with 95% alcohol alone, care being taken to prevent the admission of air to the reaction vessel. The tube C was now broken and the black solid, covered with alcohol, removed to a tube where it was washed several times by decantation with alcohol and finally dried *in vacuo*. The black crystals were analyzed for potassium, molybdenum, cyanogen content and water. The potassium was obtained as potassium sulfate and the molybdenum as lead molybdate from separate solutions made by decomposing 0.25-g. samples of the compound with concentrated nitric acid, evaporating to dryness, and by subsequently dissolving the residue in water. The molybdenum was removed as barium molybdate in the procedure for the determination of the potassium. The cyanide content was determined by the method of Bellucci and

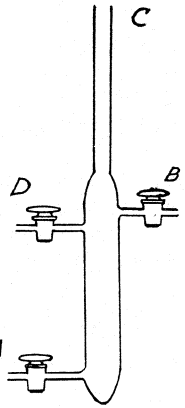


Fig. 1.—Apparatus for the preparation of $K_4Mo(CN)_7\cdot 2H_2O$ in the presence of nitrogen.

Ricca.[3] The water was obtained by the heating of 1-g. samples in a current of dry oxygen at 300°, the moisture being collected in a weighed calcium chloride-Marchand tube.

The results of the above analyses were: K, 33.24, 33.29; Mo, 20.53, 20.30; CN, 38.52, 38.59; $H_2O$, 7.60, 7.87. These results point to the formula, $K_4Mo(CN)_7 \cdot 2H_2O$, the theory for which requires: K, 33.24, Mo, 20.41; CN, 38.69; $H_2O$, 7.66. It is likely that one or both molecules of water are in the complex giving the molybdenum a coördination number of eight.

As a test for the valency of the molybdenum, the procedure of Collenberg[4] was followed, who examined the octacyanide. A sample of the heptacyanide, weighing 0.3295 g., was oxidized with hot ferric alum solution in the presence of mercuric sulfate, the molybdenum being oxidized to the hexavalent condition. The ferrous salt formed was titrated with standard permanganate solution; 2.20 milliequivalents of permanganate were used, the theoretical for $Mo^{+3} \longrightarrow Mo^{+6}$ being 2.10 milliequivalents and for $Mo^{+4} \longrightarrow Mo^{+6}$, 1.4 milliequivalents. Subsequent determinations checked these results and the conclusion must be drawn that the compound is one of trivalent molybdenum.

The coördination number of molybdenum is represented in this compound at eight as in the other cyanides of molybdenum of valence four and five, $K_4Mo(CN)_8 \cdot 2H_2O$ and $K_3Mo(CN)_8$. Attempts to prepare a complex cyanide of trivalent molybdenum in which the molybdenum would have a coördination number of six, by the use of an amount of potassium cyanide smaller than that required for the complete reaction with the complex hexachloride, resulted in the same black heptacyanide.

Potassium molybdenum heptacyanide dihydrate gradually changes in moist air to the yellow octacyanide. It is very soluble in water, forming a brown solution which on great dilution becomes pink, the color one associates with other anions of complex molybdenum salts containing trivalent molybdenum. Potassium permanganate is reduced by the heptacyanide and the yellow color of the $Mo(CN)_8^{---}$ ion first appears, only to be destroyed by further addition of permanganate. With alkalies black molybdenum trihydroxide is formed. Colored precipitates were obtained when solutions of the heptacyanide were treated with the following solutions, air being excluded in these tests: with lead acetate, red-brown; with zinc sulfate, gray; with manganese sulfate, grayish-green; with cobalt chloride, dark gray; with nickel chloride, green; with copper sulfate, dark purplish-brown; with ferrous sulfate, light blue.

Work is now in progress in this Laboratory on the corresponding complex cyanide of tungsten.

## Summary

By allowing $K_3MoCl_6$ to react with potassium cyanide solution at room temperature and in the presence of nitrogen there is produced a complex cyanide of trivalent molybdenum, analyses of which correspond to a formula of $\overrightarrow{K_4}\left[Mo\begin{matrix}(CN)_7\\H_2O\end{matrix}\right]\cdot H_2O$, as does the quantitative examination of its reducing power.

The fact that potassium thiocyanate reacts in the presence of air with $K_3MoCl_6$ solution to produce $K_3Mo(SCN)_6$ while under like conditions potassium cyanide reacts to give $K_4Mo(CN)_8$ is accounted for by assuming an intermediate formation of $Mo(OH)_3$, due to the alkali formed by the hydrolysis of the cyanide. This hydroxide is readily oxidized in the air

[3] Bellucci and Ricca, *Atti congresso naz. chim. pura applicata*, 476 (1923).

[4] Collenberg, *Z. anorg. allgem. Chem.*, **121**, 310 (1922).

to the brown dioxide. Both the trivalent hydroxide and the dioxide are dissolved by long heating with a solution of potassium cyanide in contact with air, and give the octacyanide. The fact, too, that in the presence of nitrogen a solution of $K_3MoCl_6$ and potassium cyanide react, when heated, to form $K_4Mo(CN)_8$ was made clear after it was noted that $K_3MoCl_6$ in alkaline solution, when heated in the absence of oxygen, reacts with the water, the molybdenum being oxidized and hydrogen being evolved.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

# AN EQUATION FOR ELECTROLYTIC CONDUCTANCE

BY THEODORE SHEDLOVSKY

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Debye and Hückel[1] have proposed a theory for the effect of the ionic atmosphere on the mobilities of ions. According to that theory the decrease in equivalent conductance should be proportional to the square root of the concentration, a relation which was first found empirically by Kohlrausch. The theoretical calculations for the decrease of ionic mobility with increasing concentration consider two effects. In the first place, when an ion moves through a solution under the influence of an applied electric field, it tends to disturb the surrounding ionic atmosphere, which then exerts an opposing electric force. In the second place, the ions comprising the ionic atmosphere produce a counter current of solvent which also retards the motion of the central ion.

However, Onsager[2] has pointed out that in calculating the first or so-called ionic effect, Debye and Hückel neglected to take into account the influence of the Brownian movement of the ions, and also used a treatment which is valid only if the negative and positive ions have equal mobilities. Furthermore, he has shown that the second or electrophoretic effect could be calculated in a manner which does not involve the ionic radii. Onsager's treatment likewise confirmed the square-root relationship between the equivalent conductance decrease and concentration, and, what is very important, the proportionality factor in his theoretical expression can be readily calculated from well-known constants.

Although Onsager's equation has been shown to be in close agreement with measurements at very low concentrations, it is strictly valid only as a limiting expression. This is so because in the derivation of the simple equation, only the first approximations were retained in the mathematical

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

[2] Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

treatment, and also the simple physical picture assumed in the derivation may be inadequate for finite concentrations.

Numerous empirical equations have been proposed to correlate conductance measurements with concentration, and to serve for extrapolations of equivalent conductances at infinite dilution. An empirical formula suitable for the latter purpose should, if the recent theoretical deductions are correct, reduce in the limit of zero concentration to the Onsager equation.

Recently Ferguson and Vogel[3] and Lattey[4] have proposed conductance formulas, which, however, do not appear to be satisfactory for the purpose of extrapolation. These formulas have been criticized by Davies and others.[5]

In this paper an equation is suggested which is an empirical extension of Onsager's limiting expression, containing only one additional (empirical) constant. It agrees with measurements up to a concentration of about one-tenth normal, and yields Onsager's equation in the limit.

## The Onsager Equation

Onsager's equation for the mobility of an ion is

$$l = l^0 - \left[\frac{(0.9838)(10^6)}{(DT)^{3/2}} wl^0 + \frac{28.95\,Z}{(DT)^{1/2}\eta}\right]\sqrt{(Z_1 + Z_2)C} \qquad (1)$$

$l^0$ is the mobility at infinite dilution
$D$ is the dielectric constant of the solvent
$T$ is the absolute temperature
$\eta$ is the viscosity of the solvent
$Z$ is the charge carried by the ion (absolute value)
$C$ is the equivalent concentration
$Z_1$ and $Z_2$ are the charges carried by the anions and cations
$l_1^0$ and $l_2^0$ are the mobilities at infinite dilution of anions and cations

$$w = Z_1 Z_2 \frac{2q}{1 + \sqrt{q}}; \quad q = \frac{Z_1 Z_2 (l_1^0 + l_2^0)}{(Z_1 + Z_2)(Z_2 l_1^0 + Z_1 l_2^0)}$$

The first term in the brackets takes account of the ionic effect, and the second term of the electrophoretic effect, both of which decrease the mobility of the ions. For the equivalent conductance, $\Lambda$, of a uni-univalent electrolyte the expression

$$\Lambda = \Lambda_0 - \left[\frac{5.78 \times 10^5}{(DT)^{3/2}} \Lambda_0 + \frac{58.0}{(DT)^{1/2}\eta}\right]\sqrt{2C} \qquad (2)$$

in which $\Lambda_0$ is the equivalent conductance at zero concentration, is thus obtained.

Since, as has already been noted, all higher terms have been neglected in the derivation of this equation, it is, strictly speaking, a limiting formula. The effect of retaining higher terms, however, would be such as to decrease

[3] Ferguson and Vogel, *Phil. Mag.*, **50**, 971 (1925); **4**, 1, 233, 300 (1927); **5**, 199 (1928).

[4] Lattey, *ibid.*, **4**, 831 (1927).

[5] Davies, "The Conductivity of Solutions," John Wiley and Sons, Inc., New York, 1930, pp. 81–85, 113; *Trans. Faraday Soc.*, **27**, 597 (1931).

the rate at which $\Lambda$ falls off with concentration according to the above equation. This is in accord with the facts for strong electrolytes, and Debye and Hückel and also Onsager have used an additional empirical term, linear with concentration, for purposes of extrapolating for $\Lambda_0$ from measurements of dilute solutions. However, this extension is valid only to concentrations of several thousandths normal. If, on the other hand, the electrolyte had a tendency to associate as the concentration is increased, the observed deviations from the values predicted by Equation 2 would be in the opposite direction.

For convenience let us rewrite Equation 2 in simpler form

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C} \qquad (3)$$

where $(\alpha\Lambda_0 + \beta) = A$ is the limiting theoretical slope. Solving for $\Lambda_0$ we obtain

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} \qquad (4)$$

which is, of course, only another way of writing the Onsager equation.

For solutions in water at 25° $\alpha$ is 0.2274 and $\beta$ is 59.79, using the recent data of Drake, Pierce and Dow[6] and of Wyman[7] for the dielectric constant of water, and the values given in the "International Critical Tables" for the other constants. At 18° $\alpha$ is 0.225 and $\beta$ is 50.3.

## An Extension of the Onsager Equation

In examining the conductivity of numerous strong uni-univalent electrolytes it was found that values of $\Lambda_0$ as calculated from Equation 4 are not constant over any appreciable concentration range. Thus the data do not follow the limiting Onsager equation. However, I have observed that these computed values, which will be designated by $\Lambda_0'$, plotted against the first power of the concentration, usually give straight lines up to about 0.1 normal. On this basis the correct $\Lambda_0$ value for each electrolyte is the intercept of the $\Lambda_0'$ *vs.* $C$ line at $C = 0$. Figure 1 shows plots of $\Lambda_0'$ *vs.* $C$ for aqueous solutions of a number of strong electrolytes at 18°. The data are taken from the "International Critical Tables" and from the results of Kohlrausch and his co-workers. Figure 2 shows the same relationship for solutions of several electrolytes at 25°, the data for which have been obtained in this Laboratory with an improved conductivity technique.[8] If the slope of these lines is represented by $B$, we have the following conductance equation

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} - BC \qquad (5)$$

instead of the limiting equation (4).

[6] Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

[7] Wyman, *ibid.*, **35**, 623 (1930).

[8] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

It is an interesting fact that for many electrolytes the slopes $B$ of these lines have values not far from the magnitude of $A = \alpha\Lambda_0 + \beta$, in Onsager's limiting equation (Equation 3).

An examination of Equation 5 shows that it approaches the limiting equation of Onsager asymptotically. $\alpha$ and $\beta$ are the theoretical constants

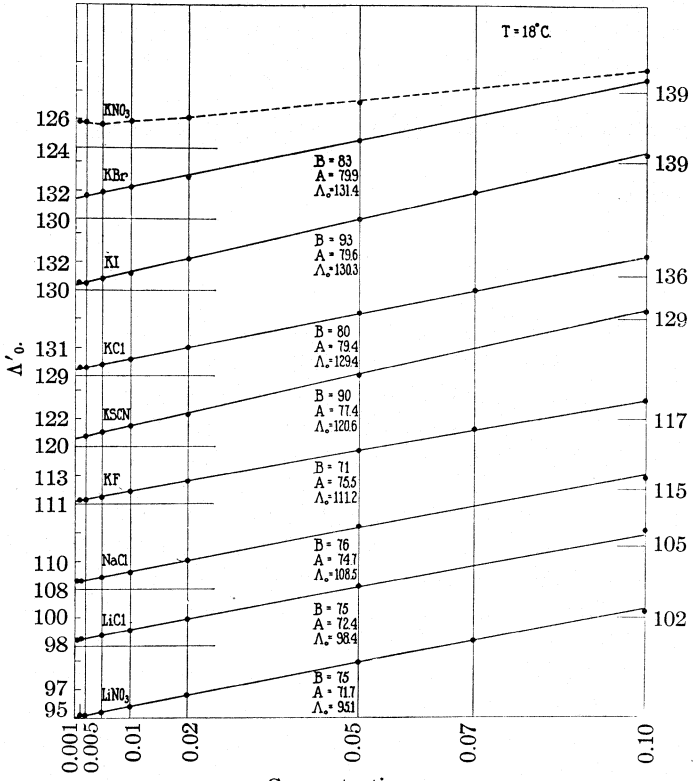


Fig. 1.

of Onsager's equation. It should be noted that Equation 5 is not equivalent to the addition of a linear term in the direct expression for equivalent conductance; *i. e.*, $\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C} + BC$, which, as mentioned above, has been used by Onsager for extrapolating $\Lambda_0$ from measurements at concentrations below 0.01 normal. The expression just given rearranges to

$$\Lambda_0 = \frac{\Lambda + BC + \beta\sqrt{C}}{1 - \alpha\sqrt{C}}$$

instead of Equation 5, in which the term $BC$ is added to $\Lambda_0$ instead of to $\Lambda$.

The substances which conform to Equation 5 (Figs. 1 and 2) belong to the class of strong electrolytes, which according to the modern theory

of solutions are considered to be essentially entirely ionized. It is found that for these cases $A$ is generally somewhat smaller than $B$ but within 15% of it.

However, in the plot for potassium nitrate, represented by the dotted curve in Fig. 1, the linear relationship between $\Lambda_0'$ and $C$ of Equation 5 does not hold. Similar behavior is exhibited by the chlorates and iodates, and

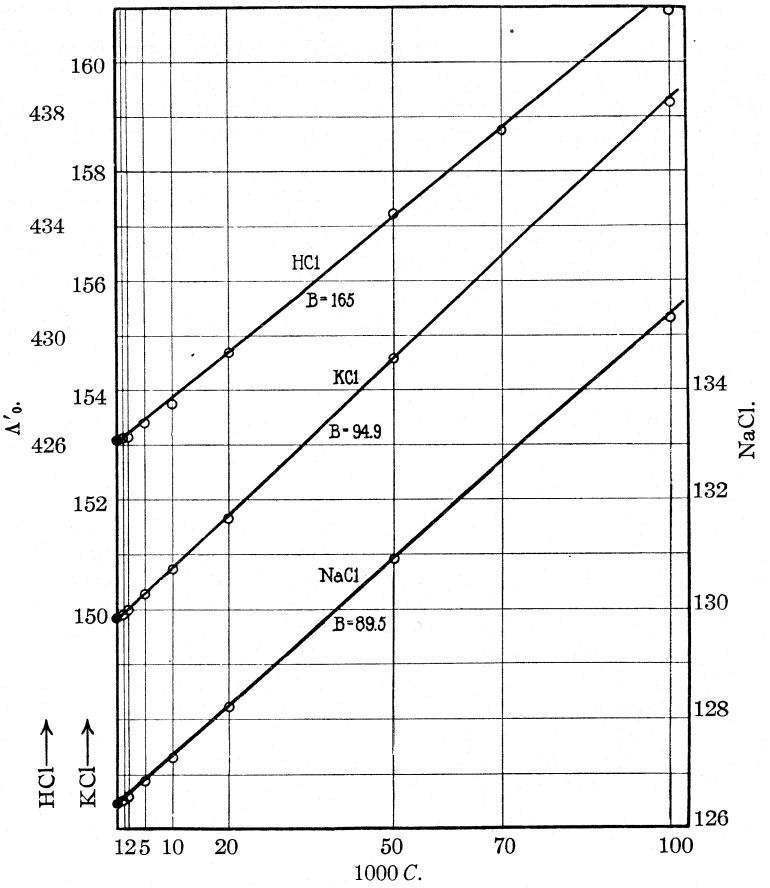


Fig. 2.

by thallium salts. We may tentatively assume that Equation 5, with $B$ near to or larger than $A$, represents the behavior of strong uni-univalent electrolytes. On this basis the substances resembling potassium nitrate behave in a manner which would result from association. Equation 5 may also be useful as a guide in calculating degrees of dissociation.

It is often more convenient to deal with an expression explicit in $\Lambda$. For this purpose Equation 5 can be rearranged in the form

$$\Lambda = \Lambda_0 - A\sqrt{C} + BC(1 - \alpha\sqrt{C}) \qquad (6)$$

where $A = \alpha\Lambda_0 + \beta$.

Table I shows a comparison between the observed values of the equivalent conductance, $\Lambda$, and those calculated from Equation 6 for the solutions of salts at 18° corresponding to the linear plots in Fig. 1. The agreement is within the limits of experimental error for these data.

TABLE I

EQUIVALENT CONDUCTANCE (18°). COMPARISON OF OBSERVED AND COMPUTED VALUES

| | $LiNO_3$ | | LiCl | | NaCl | | KF | |
|---|---|---|---|---|---|---|---|---|
| $C$ | Calcd. | Obs. | Calcd. | Obs. | Calcd. | Obs. | Calcd. | Obs. |
| 0 | 95.1 | | 98.4 | | 108.5 | | 111.2 | |
| 0.001 | 92.9 | 92.9 | 96.2 | 96.2 | 106.2 | 106.3 | 108.9 | 108.9 |
| .002 | 92.0 | 92.0 | 95.3 | 95.3 | 105.3 | 105.3 | 108.0 | 107.9 |
| .005 | 90.4 | 90.3 | 93.7 | 93.6 | 103.6 | 103.5 | 106.2 | 106.2 |
| .01 | 88.6 | 88.6 | 91.9 | 91.8 | 101.7 | 101.7 | 104.4 | 104.3 |
| .02 | 86.5 | 86.4 | 89.6 | 89.6 | 99.4 | 99.4 | 102.0 | 101.9 |
| .05 | 82.6 | 82.7 | 85.9 | 85.9 | 95.4 | 95.5 | 97.7 | 97.7 |
| .07 | 81.1 | 81.1 | .. | .. | ... | ... | 95.9 | 96.0 |
| .10 | 79.4 | 79.2 | 82.7 | 82.8 | 92.0 | 91.8 | 94.0 | 94.0 |
| A | 71.7 | | 72.4 | | 74.7 | | 75.5 | |
| B | 75 | | 77 | | 76 | | 71 | |

| | KSCN | | KCl | | KI | | KBr | |
|---|---|---|---|---|---|---|---|---|
| $C$ | Calcd. | Obs. | Calcd. | Obs. | Calcd. | Obs. | Calcd. | Obs. |
| 0 | 120.6 | | 129.4 | | 130.3 | | 131.4 | |
| 0.001 | 118.3 | 118.4 | 127.0 | 127.1 | 127.9 | 128.0 | 129.0 | 129.1 |
| .002 | 117.3 | 117.4 | 126.0 | 126.0 | 126.9 | 127.0 | 128.0 | 128.0 |
| .005 | 115.5 | 115.5 | 124.2 | 124.2 | 125.1 | 125.1 | 126.2 | 126.1 |
| .01 | 113.7 | 113.7 | 122.2 | 122.2 | 123.3 | 123.2 | 124.2 | 124.1 |
| .02 | 111.4 | 111.3 | 119.8 | 119.7 | 120.8 | 120.8 | 121.7 | 121.6 |
| .05 | 107.6 | 107.5 | 115.5 | 115.5 | 116.9 | 117.0 | 117.5 | 117.5 |
| .07 | 106.0 | 106.1 | 113.6 | 113.6 | 115.4 | 115.5 | ... | ... |
| .10 | 104.5 | 104.5 | 111.7 | 111.8 | 113.8 | 113.8 | 113.9 | 114.0 |
| A | 77.4 | | 79.4 | | 79.6 | | 79.9 | |
| B | 90 | | 80 | | 93 | | 83 | |

Table VI of the following paper shows the same comparison for our own measurements at 25° on solutions of potassium chloride, sodium chloride and hydrochloric acid.[8]

Equation 6 is consistent with the theoretical prediction of Onsager[2] that the first higher order term in his derivation, were it not neglected, would be linear in concentration and opposite in sign to the square root term.

Lattey's equation,[4] which is $\Lambda = \Lambda_0 - (A'\sqrt{C})/(1 + B'\sqrt{C})$ (in which $\Lambda_0$, $A'$ and $B'$ are adjustable constants), when applied to data on strong uni-univalent electrolytes does not necessarily approach Onsager's limiting equation. In fact Lattey's $A'$ is usually found to be appreciably greater than the theoretical limiting slope, $A = \alpha\Lambda_0 + \beta$. Also, as an extrapola-

tion formula it gives values for $\Lambda_0$ which appear to be too high, if Onsager's expression is valid for sufficiently low concentrations.

The equation proposed in this paper is an extension of Onsager's theoretical equation. It has been found to be valid up to a concentration of about tenth normal. As an extrapolation formula for most strong uni-univalent electrolytes it gives values of $\Lambda_0$ from data at concentrations which can be measured readily. These $\Lambda_0$ values will agree with values obtained from Onsager's equation applied to measurements on sufficiently dilute solutions.[9]

## Summary

An equation is proposed for the relation between the equivalent conductance of strong uni-univalent electrolytes and the concentration. It has been found to agree with measurements up to about 0.1 normal in aqueous solutions. Besides theoretically calculable constants and the limiting conductance, $\Lambda_0$, it contains only one additional constant, and reduces to the limiting Onsager equation.

[9] The author has made some preliminary tests of Equation 5 on strong uni-bivalent electrolytes. It appears to hold in a perfectly analogous manner for these cases if the concentrations are expressed as "ionic strengths." The application of the equation to this and higher valence types will be communicated at a later date to THIS JOURNAL.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

# THE ELECTROLYTIC CONDUCTIVITY OF SOME UNI-UNIVALENT ELECTROLYTES IN WATER AT 25°

BY THEODORE SHEDLOVSKY

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## Introduction

It has appeared important to obtain accurate values for the electrolytic conductance of solutions of a number of electrolytes. Besides providing a test for the conductivity relationships predicted by the modern theory of ionic solutions, such measurements make possible the calculation of the degrees of dissociation of certain weak electrolytes, as is shown in another paper.[1] Also, when combined with determinations of transference numbers, they give values for individual ionic mobilities. This will be the subject of a communication from this Laboratory in the near future.

With the alternating current bridge method, which has been almost universally used since Kohlrausch for measuring electrolytic conductance, a sensitivity of one part in 100,000 in the resistance readings can be readily attained. Due to various sources of error, some of which will be men-

[1] MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

tioned below, the accuracy of such measurements may not reach one part in 1000. In fact there are comparatively few measurements available for which a consistent accuracy of more than several hundredths of one per cent. has actually been attained.

In this paper new measurements are reported on the conductivity of several uni-univalent electrolytes in water at 25°, covering a concentration range from about $2 \times 10^{-5}$ to 0.1 normal. They were obtained with an apparatus and a technique designed to give a consistent accuracy of one or two hundredths of a per cent. for the relative conductance values.

## Experimental

**Bridge, etc.**—The alternating current bridge, oscillator, and detector used in this research have been described by the author in a previous paper.[2] With this apparatus it is possible to make measurements at several frequencies. This is important because most of the electrical errors change with the frequency, providing a useful criterion for detecting such errors.

It was shown in the earlier paper that the sources of error in the bridge (apart from the calibration of the rheostat) amounted to less than 0.002% when the direct current values of metallic resistances were compared with the corresponding a. c. measurements up to 3000 cycles. The coils in the rheostat were frequently calibrated against several Bureau of Standards standard resistances which had been certified by the Bureau of Standards, and the relative accuracy of these calibrations is a few hundredths of an ohm for the individual coils. The coils of 1000 ohms or over were immersed in a thermostat to avoid temperature fluctuations.

In measuring very dilute solutions, when cell resistances are greater than 10,000 ohms, I have found it expedient to shunt the cell with a 10,000-ohm resistance, free from reactance errors at the frequencies used. By measuring first this shunt resistance, and then the parallel combination of the cell and the shunt, the resistance of the cell is readily calculated from the relation $\rho = SR/(S-R)$ in which $\rho$ is the desired resistance of the cell, $S$ the resistance measurement of the shunt and $R$ the resistance measurement of the parallel combination. Of course, the use of such a shunt method results in a loss of precision. However, $S$ and $R$ are both known to 0.1 ohm, since the bridge easily has that sensitivity when measuring resistances of the order of 10,000 ohms, and the calibrations of the individual coils are accurate to 0.05 ohm, as mentioned above. Consequently, an accuracy of 0.01% is retained when $S-R$, the determining factor, amounts to 1000 ohms, which corresponds to a resistance of about 90,000 ohms in the cells. That this method has the precision just stated was shown by making check measurements with shunts differing in resistance by 2000 ohms.

[2] Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

**Conductivity Cells.**—Jones and Bollinger[3] have shown in a recent paper that many cells which are commonly used in careful conductivity work suffer from a source of error inherent in the design. In such cells, in which the filling tubes are relatively close to the electrode leads, disturbing parasitic currents can flow through capacity–resistance paths, and these can produce apparent variations in cell constants. A variation of cell constant at high resistances had been observed by Parker,[4] who attributed the effect to adsorption. Jones and Bollinger have, however, definitely proved that this so-called "Parker effect" disappears when the filling tubes and electrode leads in the cells are spaced in a manner which avoids appreciable stray currents. Their new cells, which are designed with this in view, give measurements which are constant at several frequencies, indicating that this type of error has been eliminated. The measurements I have made on solutions of concentrations greater than 0.005 normal were carried out in cells of the type recommended by these authors. These cells were made from Jena $16^{III}$ glass and the electrodes were lightly platinized.

With very dilute solutions it is desirable to use a cell of relatively large volume, so that increasing concentrations can be built up and successively measured without risk of contamination from atmospheric or other impurities. Cells of this type have been described by Weiland,[5] Kraus and Parker,[6] Hartley and Barrett,[7] and have been generally used in recent work on dilute solutions. These workers used cells consisting essentially of a flask with a pair of dipping electrodes as is represented diagrammatically in Fig. 1 (a). However, as Jones and Bollinger have pointed out, dipping electrodes may also lead to errors in conductivity measurements. The following brief analysis will make clear the reason for such errors and the direction of their effect on the measurements.

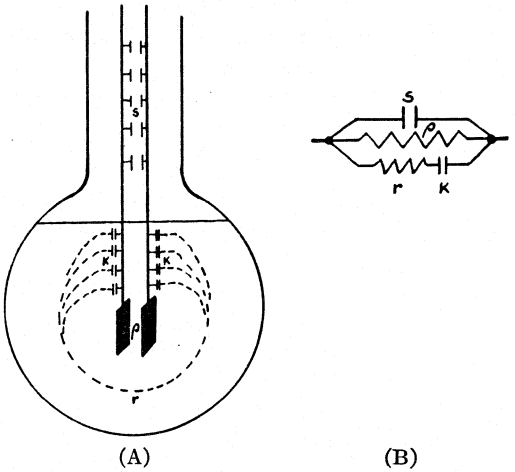


Fig. 1.

With the cell indicated in Fig. 1 (a) the total current measured in the

[3] Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).
[4] Parker, *ibid.*, **45**, 1366, 2017 (1923).
[5] Weiland, *ibid.*, **40**, 133 (1918).
[6] Kraus and Parker, *ibid.*, **44**, 2429 (1922).
[7] Hartley and Barrett, *J. Chem. Soc.*, **103**, 786 (1913).

bridge consists, when polarization is negligible, not only of the current flowing directly between the electrodes through the solution and a capacity current between the electrodes (including the leads), but there is also a parasitic current which flows from the electrode leads by electrostatic capacity to the solution and then through it. This latter current is neither constant nor directly proportional to the resistance of the solution, and thus tends to produce apparent variations in the cell constant.

The electrical circuit for the cell in Fig. 1 (a) is shown sufficiently closely for our purpose by the accompanying diagram Fig. 1 (b). Since this circuit is balanced in the bridge by a resistance and a capacity in parallel, we have the following condition at balance[8]

$$\frac{1}{R} + j\omega c = \frac{1}{\rho} + j\omega S + \frac{1}{r - j/\omega\kappa} \tag{1}$$

in which $\rho$ is the resistance of the solution between the electrodes, $S$ the electrostatic capacity between the electrodes including their leads, $r$ and $\kappa$ are the resistance and capacity components of the disturbing parasitic current, $R$ is the resistance reading and $c$ the capacity reading in the bridge, $\omega$ the angular frequency, and $j$ the reactance operator.

Solving Equation 1 for $1/R$ we obtain

$$\frac{1}{R} = \frac{1}{\rho} + \frac{1}{r + (1/\omega^2\kappa^2 r)} \tag{2}$$

Since $r$ depends on the resistance of the solution, it is directly proportional to $\rho$, that is, $r = a\rho$, where $a$ is a constant. Thus

$$\frac{1}{R} = \frac{1}{\rho}\left(1 + \frac{1}{a + (1/\omega^2\kappa^2 a\rho^2)}\right) \tag{3}$$

which, on expansion, neglecting higher terms, gives

$$\frac{1}{R} = \frac{1}{\rho}\left(1 + \frac{1}{a} - \frac{1}{\omega^2\kappa^2 a^2\rho^2}\right) \tag{4}$$

The term $1/\omega^2\kappa^2 a^2\rho^2$ which we shall call $d$ varies with the square of the frequency and the square of the resistance of the solution.

It is evident from this treatment that a parasitic current resulting from a path consisting of a capacity in series with a resistance such as $r$ and $\kappa$ in Fig. 1 will produce errors in the conductivity measurements if balanced, as in the usual bridge, with a resistance and a pure capacity. However, no error results from a shunting current in the cell through a pure capacity such as $S$ in the same figure. Since the correction terms in Equations 3 and 4, arising from the disturbing parasitic current, contain factors not readily determined, it is better to design cells so as to eliminate such currents, rather than to attempt to correct for them.

Equation 4 accounts for the observation that measurements made with dipping electrodes vary with the frequency. Furthermore, if the cell

[8] See, for instance, Hague, "Alternating Current Bridge Methods," p. 71.

is calibrated with a solution having a resistance $\rho_0$ for which the term $1/\omega^2\kappa^2a^2\rho^2 = d_0$, measurements at higher resistances or higher frequencies will result in conductance values which are apparently too high, since $d$ will decrease progressively with increasing resistance or frequency. And, by similar reasoning, the apparent conductances will be too low for resistances less than $\rho_0$.

To avoid this error I have constructed cells in which disturbing parasitic currents are not present. Such a cell is shown in Fig. 2 (a). In this design, which includes Jones and Bollinger's recommendations, the electrodes are taken out of the flask, the leads to the electrodes are separated from each other and the space between is filled not with the solution but with the oil in the thermostat. Consequently the disturbing parasitic currents are made negligible. The lead M, nearest to the flask, is connected to the terminal of the bridge which is maintained at earth potential, so that capacity effects to earth from this relatively large surface are avoided. It has been found on repeated tests that conductance values obtained with this cell are independent of frequency, between 1000 and 3000 cycles.

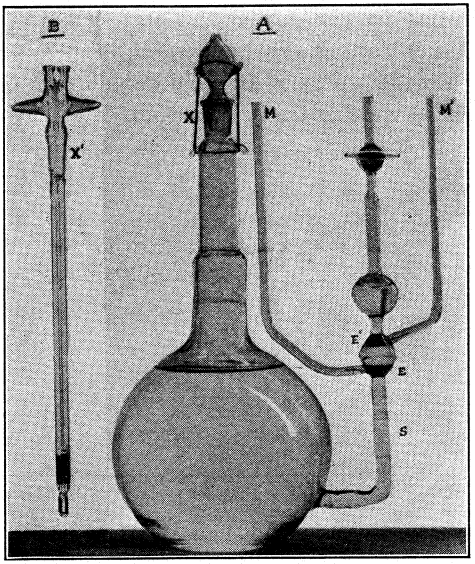


Fig. 2.

As an experimental proof of the electrical error due to dipping electrodes Fig. 2 (b) measurements with them have been compared with corresponding ones made in the cell shown in Fig. 2 (a), using the same solutions. The dipping electrodes were firmly set into the flask of the cell shown in Fig. 2 (a) through the ground joint x–x′. The results of the comparison are shown graphically in Fig. 3. In this plot the ordinates correspond to the ratio of values obtained with the dipping electrodes Rd and those obtained with our cell R. The abscissas correspond to the resistance as measured by the immersed electrodes. Since the readings obtained with the cell shown in Fig. 2 (a) are independent of frequency, they are considered to be correct. On this basis the curves in Fig. 3 represent the apparent variations of the cell constant of the dipping electrode with resistance at the frequency indicated. In accord with Equation 4 the variation increases with the resistance and the frequency.

Some further essential details of the design of the cell shown in Fig. 2 (a) are as follows. The flask, of transparent quartz, has a capacity of 1 liter. The cell proper is made of Jena $16^{III}$ glass connecting to the flask through a graded seal S. The electrodes E, E′ are truncated hollow cones of platinum foil, the outer surfaces of which are completely sealed to the glass. They are platinized only to a dull gray color, which is sufficient to avoid polarization at the concentrations used in this cell. Electrical contact is made with the electrodes through the mercury cups M, M′, which are amply spaced to avoid parasitic shunting currents. To eliminate temperature errors the leads from the cups extend into two short test-tubes of mercury supported in the thermostat. Two additional leads connect these tubes to the bridge. Three cells of this design of somewhat different dimensions have been used in measuring dilute solutions of potassium chloride and sodium chloride. The conductance values obtained in all three were entirely consistent with each other.

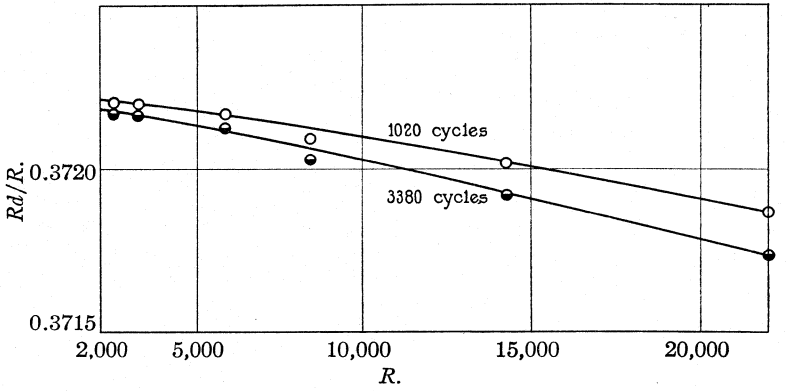


Fig. 3.

**Temperature Control.**—The temperature of the solutions measured was controlled by immersion of the cells in an electrically operated thermostat filled with a light mineral oil. Jones and Josephs[9] pointed out that appreciable errors may result from the use of water in the thermostat in measurements with alternating currents. The regulator consists of a hollow-walled cylindrical steel tube filled with about 300 cc. of mercury, connecting to a glass capillary in which is set the regulating needle. By use of a radio tube arrangement, similar to that described by Beaver and Beaver,[10] sparking at the mercury surface is entirely avoided. The heater consists of bare manganin wire wound non-inductively on an insulated frame around the regulator. The temperature of the thermostat, which remained constant to ±0.001°, was set accurately at 25° (±0.001°) with

[9] Jones and Josephs, THIS JOURNAL, **50**, 1065 (1928).

[10] Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

the aid of a carefully calibrated platinum resistance thermometer, which serves as a temperature standard in this Laboratory. It is of the strain-free type, with a resistance of about 25 ohms and is provided with a special thermostated Mueller thermometer bridge and a sensitive galvanometer.

## Purification of Materials

**Conductivity Water.**—The conductivity water was obtained by redistilling distilled water from alkaline potassium permanganate in a still similar to the one described by Kraus and Dexter.[11] The precautions suggested by these authors were carefully observed. In this apparatus the steam from the evaporator passes through a settling chamber in which traces of spray are separated from the vapor. This vapor then passes to a condenser where it is partially condensed. The large volume of uncondensed vapor carries with it most of the carbon dioxide and other gaseous impurities. The condensed water was collected out of direct contact with air in a 15-liter "Vitreosil" quartz flask.[12] This flask was fitted with an air-tight block tin cover carrying block tin pipes for collecting and withdrawing the water. The conductivity water in this container was protected from atmospheric impurities by a set of "guard" bottles, containing sulfuric acid and strong potassium hydroxide solution, followed by a long tube filled with soda lime. The specific conductance of the water was between 0.1 and 0.4 $\times 10^{-6}$ mhos.

**Sodium and Potassium Chlorides.**—The best obtainable C. P. salts were crystallized once by absorbing pure hydrochloric acid gas in a hot saturated solution which was gradually cooled to 0°. After centrifuging, the product was recrystallized from conductivity water, again centrifuged, and dried in a clean electric oven. Two samples of potassium chloride were prepared by four crystallizations from conductivity water, but no difference was observed between the conductance of solutions made with them and with the samples prepared as above. The purified salts were fused in platinum under vacuum in an electric furnace. When potassium chloride and particularly sodium chloride is fused in air, the resulting product is slightly alkaline, as can be seen from a pink fringe around a crystal placed in a few drops of distilled water containing a trace of phenolphthalein. However, fusing the salts in vacuum avoids this difficulty, probably by removing traces of water quickly enough to prevent appreciable hydrolysis at the high temperatures.

**Potassium Nitrate and Silver Nitrate.**—The C. P. salts[13] were recrystallized several times from conductivity water, centrifuged, dried and fused as above. The fused salts gave negative tests with phenolphthalein and with acidified potassium iodide and starch solution, showing that no loss or decomposition of nitrate took place.

A "Richard's bottling apparatus,"[14] was used in handling the fused salts, since they are more or less hygroscopic. With this apparatus[15] it is possible to fuse salts in a controlled atmosphere, and to transfer them into glass-stoppered weighing bottles where they may be kept without risk of contamination from the air.

**Hydrochloric Acid.**—Constant boiling hydrochloric acid was prepared from C. P.

[11] Kraus and Dexter, THIS JOURNAL, **44**, 2469 (1922).

[12] In the measurements on hydrochloric acid (dilute) the conductivity water was collected directly from the still into the cell. Its conductivity was always less than $2 \times 10^{-7}$.

[13] A pure sample of silver nitrate was kindly supplied by Dr. Vinal of the Bureau of Standards. This sample was recrystallized once from conductivity water.

[14] T. W. Richards and H. G. Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 59 (1896).

[15] This excellent apparatus, which is essential for accurate work with hygroscopic materials, has not come into as general use as might be desired.

acid in the manner described by MacInnes and Dole.[16] The barometric pressure corresponding to the fraction of acid collected was carefully noted, and the concentration of the product was thus determined from the data of Foulk and Hollingsworth.[17] Analyses were also made by differential potentiometric titrations (through a sodium hydroxide solution) against benzoic acid and potassium hydrogen phthalate with the procedure described by MacInnes and Cowperthwaite.[18] The three methods agreed well within 0.01%. Although the distilled acid, which was stored in small glass-stoppered Pyrex flasks, showed no appreciable change in concentration on standing for several weeks, fresh samples were taken for making up the solutions used in this work.

**Determination of Cell Constants.**—The "Jones and Bollinger"[3] cell for moderately concentrated solutions (cell B) was calibrated with a 0.1 "demal" solution of potassium chloride, containing 7.47896 g. of potassium chloride and 1000 g. of water (weighed in air). The specific conductance of this solution according to Parker and Parker[19] is $0.012852_4$ at 25°. This value has been taken as the basis for all the conductance measurements reported in the present paper.

Another "Jones and Bollinger" cell (C) had a resistance of less than 600 ohms when filled with 0.1 "demal" potassium chloride solution. But since it is best to measure cell resistances of over 1000 ohms to retain the full sensitivity of the bridge, the cell C was calibrated by intercomparison with cell B. The ratio between measurements in these two cells remained constant to 0.01% over a wide range of resistances with solutions of different electrolytes, *i. e.*, no "Parker effect" was observed. The cell constants showed only slight variations with time over a period of two years. In that time the constant of cell B, $K_B$, varied between 24.706 and 24.712; and that of cell C, $K_C$, varied between 7.6342 and 7.6357. In computing the conductance values obtained in these cells, which were calibrated at intervals of two or three months, the most recent calibration was always used.

The cell constants of the "flask" cells Fig. 2 (a) which were used in measuring the very dilute solutions, were determined at the end of each run in these cells by intercomparison with cell C. Also for these cells no "Parker effect" was observed. For three cells of this type the constants were (1) 0.70652, (2) 0.51247, (3) 0.58915; cell (1) was used in series a, b, d, e on potassium chloride, and series a, b on sodium chloride; cell (2) was used in series f on potassium chloride and series c, d, e, f on sodium chloride; cell (3) was used in all the other dilute series.

**Preparation of Solutions.**—Solutions at round concentrations of 0.1, 0.05, 0.02, 0.01, 0.005 and in some cases 0.07 normal at 25° (gram moles per liter of solution at 25°) were made up by weight, using the density data given in the "International Critical Tables." The glassware was cleaned with hot dichromate–sulfuric acid solution, thoroughly rinsed with distilled water, steamed out, and dried with air which had been passed through towers of fused calcium chloride followed by a long cotton filter. After determining the dry weight of the flasks, they were again rinsed with several samples of conductivity water before being used for making up the solutions.

**Weighing.**—Three balances were used for weighing in this research. A large Christian Becker chainomatic balance with a capacity of 10 kilos and an average sensitivity of 0.5 mg. was used in weighing water for the solutions. A Christian Becker analytical balance, with a sensitivity of 0.05–0.1 mg. was used for weighings corresponding to loads between 10 and 150 g. A Kuhlman microbalance with a sensitivity of 0.001 mg. was used for weighing small quantities of solutes. All weighings were made by

[16] MacInnes and Dole, THIS JOURNAL, **51**, 1119 (1929).

[17] Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923).

[18] MacInnes and Cowperthwaite, *ibid.*, **53**, 555 (1931).

[19] Parker and Parker, *ibid.*, **46**, 332 (1924).

the tare and substitution method, and were corrected to vacuum. The weights for the large and micro balances were carefully calibrated to the same basis against a standard set which was certified by the Bureau of Standards.

## Procedure

**Measurements above 0.005 Normal.**—The conductivities of solutions above 0.005 normal, which were made up to round concentrations of 0.005, 0.01, 0.02, 0.05, 0.07 and 0.10 normal,[20] were determined in cells B and C. These cells were periodically cleaned with dichromate–sulfuric acid mixture, followed by very thorough rinsing with distilled water, and finally with conductivity water, with which they were also kept filled when not in use. Occasionally, when it was suspected that the cells had been contaminated with grease, they were cleaned with alcohol and ether before receiving the usual cleaning treatment.

The procedure was to rinse the cell used in a particular measurement with six or eight portions of the solution, and then to let the cell stand, filled with solution, for fifteen to thirty minutes. The cell was then refilled with solution and immersed in the thermostat, where it attained thermal equilibrium within about fifteen minutes, after which its resistance remained constant. Refilling the cell and repeating the measurement usually gave the same resistance value, but several fillings of the cell with check measurements were always made.

For transferring the solution from the storage flask into the cells used for the more concentrated solutions, the ground-glass stopper of the flask was replaced by a two-holed rubber stopper into which were fitted a short glass tube and a long U-shaped glass tube, the latter reaching to the bottom of the flask. The tubes were, of course, previously cleaned and dried. The outside end of the U-tube was connected to the cell, and the solution was forced into it with a sufficient pressure of purified air.

The solvent correction for the solutions measured in this manner is relatively small. It was determined by finding the conductivity of a sample of the water used in making up the solution in a cell similar in design to cells B and C, but having large electrodes and a cell constant of about 0.037. The conductance of the water used for these solutions, since it was not completely protected from the carbon dioxide in the atmosphere, was between 0.5 and $0.8 \times 10^{-6}$ mhos, usually about $0.6 \times 10^{-6}$. However, this value corresponds to about only 0.1% of the conductivity of a 0.005 normal solution for the electrolytes measured.

**Measurements of Very Dilute Solutions.**—The conductivities of the most dilute solutions were measured in the "flask" cell Fig. 2 (a). The cell, which was thoroughly cleaned in the manner described below, was partially filled with about 950 cc. of fresh conductivity water. The solvent was then swept out for several minutes with purified nitrogen entering through the stopcock and escaping through the neck of the flask. (The stopcock and ground-glass stopper in the "flask" cell were lubricated with a trace of thick, purified vaseline. This was prepared by distilling off the more volatile components of white vaseline under a vacuum, and the viscous residue was extracted repeatedly with hot conductivity water.) The cell with the water was then weighed, and the quantity of solvent was determined by subtracting the weight of the empty dry cell. After introducing mercury into the tubes leading to the cell electrodes, the cell was placed in the thermostat and connected to a source of purified nitrogen, etc., in the manner shown in Fig. 4. The mercury cup $E_1$, which is nearest to the flask and makes contact with the lower electrode in the cell proper (W), was connected to the bridge terminal at the junction of the rheostat and detector. Owing to the relatively large surface of the

[20] Check series of solutions were kindly prepared by Mr. Donald Belcher of this Laboratory.

flask, it has an appreciable capacity to earth. However, by connecting $E_1$ to the terminal which is at earth potential when the bridge is balanced, no capacity current to earth is likely from this source. The ground-glass stopper (S) was held in place with a rubber band. By means of the three-way stopcock A, the cell could be connected either to a source of purified nitrogen under a pressure, regulated by the reduction valve V, or to the atmosphere through the guard train D. With this arrangement (T open and A as in Fig. 4), the valve V was set so that a slight pressure was established in the flask (F). This pressure was regulated to force solution into the cell proper (W) past the electrodes, half filling the bulb (B) when the stopcock A was subsequently turned so as to connect T to the atmosphere (through D). Thus the cell W could be alternately filled and emptied by turning A to the proper position. With A set as in Fig. 4, the liquid in the flask could be stirred with purified nitrogen by lifting the stopper S slightly.

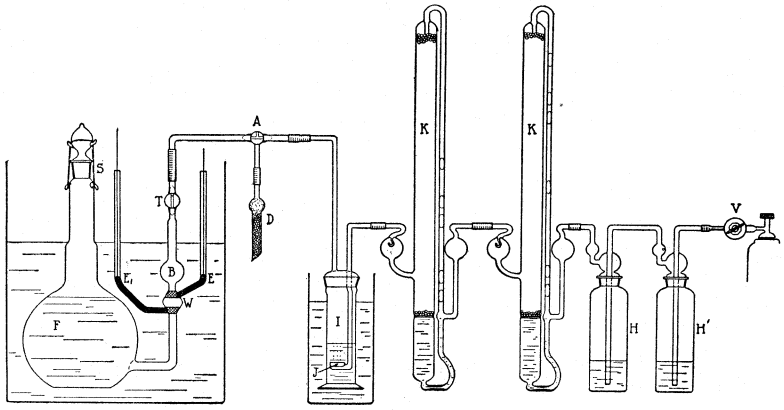


Fig. 4.

The purification train for the nitrogen consists of two gas scrubbing bottles containing sulfuric acid (H, H′), two scrubbing towers (K) of the type recommended by Kraus and Parker,[21] filled with strong potassium hydroxide solution, and finally the glass filter bottle (I) which contains conductivity water and is immersed in the thermostat. In this bottle, the gas passed through the sintered glass membrane (J) in fine bubbles, and is thus saturated with water vapor at the temperature of the thermostat.

The guard train (D) consists of a tube of sulfuric acid, and a long soda lime tube. The purpose of this train is to prevent atmospheric impurities from diffusing into the cell when it is opened to the air by the stopcock A.

After the conductivity water in the "flask" cell had reached thermal equilibrium in the thermostat, the cell proper (W) was filled, as described above, by manipulating the stopcock (A) with the stopcock (T) open. Then (T) was closed and the resistance was measured. This procedure was repeated a number of times to make sure that a reliable, constant value was obtained.

Then, with the ground-glass stopper (S) removed and a slow stream of nitrogen passing through the flask, an increment of solute was quickly added and the stopper replaced. This was added in the form of salt fused in tiny platinum cups, which were dropped into the flask, or in the form of solution of known concentration which was added from a weight buret. Two weight burets were used, one having a capacity of 1.5 cc. and the other 75 cc. Both burets were made from Pyrex glass. In the case of the

[21] Kraus and Parker, THIS JOURNAL, 44, 2432 (1922).

platinum cups, containing 20 to 90 mg. of fused salt, and the micro buret, containing a maximum of 1.5 cc. of solution, the required weighings were made on the micro balance to 0.001 or 0.002 mg. When the larger buret was used, at least 5 g. of solution was added, and the weighings were made on the analytical balance to 0.1 mg. The small platinum cups were handled with platinum-tipped tongs, the micro buret with clean, oil-free chamois, and the larger buret with clean silk gloves. For the most dilute solutions the quantities of solid required were too small to weigh accurately. In such cases small quantities of solution of known concentration were added from the micro weight buret. However, most of the values given for potassium chloride, sodium chloride and potassium nitrate were obtained with the use of the platinum cups. These weighed about 0.25 g., their exact weight being determined for each run. They were readily cleaned by rinsing in a stream of distilled water and heating to incandescence over a Bunsen burner until no color was imparted to the flame. The small amounts of salt were fused in the cups in the manner already described. After the addition of an increment of solute, the stopcock T was closed, the flask cell was disconnected, removed from the thermostat, and thoroughly shaken until all the added solute was well distributed. Then the flask was replaced in the thermostat, reconnected, and, by manipulating (A), (T) and (S), the cell proper was filled and emptied numerous times, and the solution stirred with gas. After thermal equilibrium had again been established, the solution was measured, as described above, with several refillings of the cell proper (W). This precedure was repeated until several concentrations had been built up and measured. In the case of some very low concentrations, especially with hydrochloric acid, it was found that the measured resistance for a particular filling of C changed with time. It is supposed that this effect was due to adsorption or slight contamination from the Jena glass of which the cell proper is constructed (the flask itself being of quartz). However, since the relative volume of the cell proper is small, this effect on the solution as a whole was probably negligible. In any case, reproducible values were always obtained by taking the readings immediately on filling (W), or by taking readings over a period of time and extrapolating to zero time. The level of the solution in the bulb (B) or in the flask had no detectable effect on the measurements.

After the conductance of the last solution had been determined in this apparatus, it was again measured in cell C. Using the result of this measurement, it was possible to check the constant of cell (W) at the end of each series of determinations.

Before starting a new run, the flask cell was completely cleaned inside and outside. Most of the oil adhering to the outside of the cell was removed with warm soap solution. The mercury cups were cleaned out with nitric acid. All grease was finally removed with ether, the flask and cell were completely filled with warm sulfuric acid–dichromate mixture and allowed to stand overnight. It was then thoroughly rinsed with distilled water by letting at least 5 liters flow through it, entering at the stopcock and leaving through the neck of the flask. The quartz flask was then further cleaned with steam, and rinsed with several portions of conductivity water. The outside of the flask and also the mercury cups were dried and the apparatus was ready for the next run.

## Results

All the conductance values here presented are on the basis of a specific conductance of $0.012852_4$ for a 1/10 "demal" potassium chloride solution at 25°.[19] Such a solution contains 7.47896 g. of potassium chloride in 1000 g. of water (weights in air *vs.* brass).

The equivalent conductances are defined as $\Lambda = 1000\ L/C$, $L$ being the measured specific conductance, and $C$ the concentration in equivalents per

liter of solution at 25°. The molecular weight values given in the "International Critical Tables" have been used throughout. Except in the case of the hydrochloric acid solutions, the conductance of the solvent has been subtracted from the measured specific conductances.

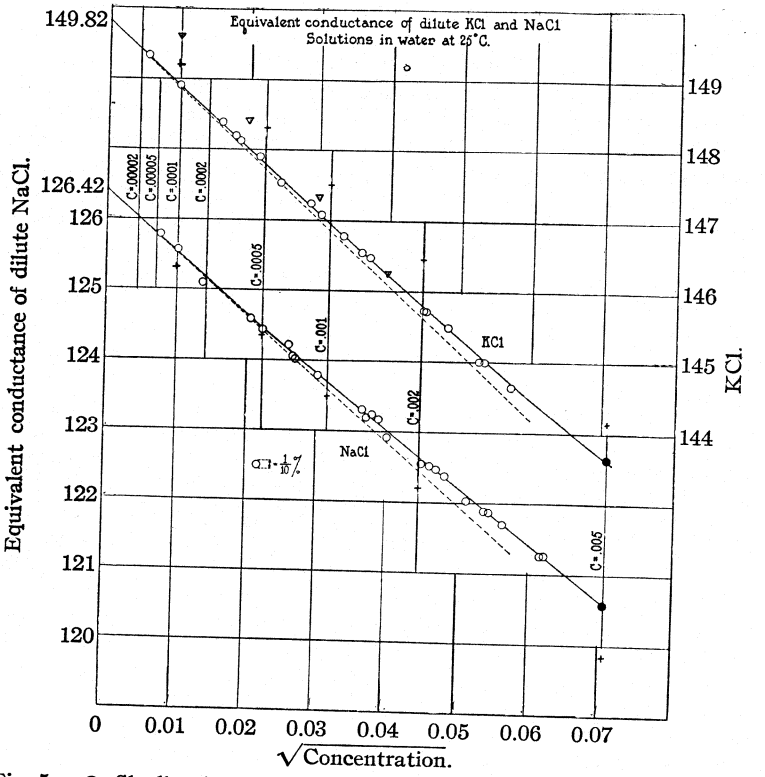


Fig. 5.—○, Shedlovsky; ▽, Grindley and Davies; +, Jeffery and Vogel.

Tables I to V give the results of the measurements on the dilute solutions (below 0.005 normal). The average values of the measurements at the round concentrations between 0.1 and 0.005 normal are given in Tables VI and VII. These two tables also give the conductivity values corresponding to round concentrations between 0.002 and 0.0001 normal, graphically interpolated from the data on the dilute solutions. Graphs corresponding to the data in the tables are shown in Figs. 5 to 8, in which the equivalent conductance is plotted against the square root of the concentration. On these graphs, the dotted lines represent the theoretical slopes (A) calculated from Onsager's conductance equation,[22] which, however, is a limiting expression, strictly only valid at infinitesimal concentrations. *It can be seen from these figures that the Onsager equation yields,*

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

TABLE I

EQUIVALENT CONDUCTANCES OF POTASSIUM CHLORIDE AT 25°

| Series | $C \times 10^4$ | $\Lambda$ | Series | $C \times 10^4$ | $\Lambda$ |
|---|---|---|---|---|---|
| f | 0.32576 | 149.33 | d | 11.321 | 146.76 |
| f | 1.0445 | 148.91 | e | 14.080 | 146.46 |
| f | 2.6570 | 148.38 | d | 15.959 | 146.26 |
| e | 3.3277 | 148.19 | b | 20.291 | 145.72 |
| b | 3.5217 | 148.12 | e | 20.568 | 145.71 |
| c | 4.6948 | 147.89 | d | 23.379 | 145.48 |
| a | 6.0895 | 147.52 | a | 27.848 | 145.00 |
| e | 8.4200 | 147.23 | e | 28.777 | 144.99 |
| c | 9.2856 | 147.07 | b | 32.827 | 144.64 |

$\Lambda_0 = 149.82$

TABLE II

EQUIVALENT CONDUCTANCES OF SODIUM CHLORIDE AT 25°

| Series | $C \times 10^4$ | $\Lambda$ | Series | $C \times 10^4$ | $\Lambda$ |
|---|---|---|---|---|---|
| e | 0.59441 | 125.79 | f | 15.306 | 123.17 |
| e | 1.1283 | 125.57 | d | 16.271 | 122.91 |
| d | 1.8985 | 125.09 | b | 20.348 | 122.54 |
| d | 4.2677 | 124.58 | c | 21.253 | 122.51 |
| f | 5.0056 | 124.44 | f | 22.275 | 122.47 |
| c | 6.7898 | 124.21 | a | 23.388 | 122.37 |
| a | 6.9196 | 124.21 | b | 26.538 | 122.02 |
| d | 7.1846 | 124.05 | c | 28.988 | 121.88 |
| b | 7.3843 | 124.02 | – | 29.806 | 121.87 |
| f | 9.2243 | 123.78 | a | 31.862 | 121.70 |
| c | 13.448 | 123.31 | c | 37.367 | 121.26 |
| b | 13.868 | 123.19 | a | 38.776 | 121.26 |
| a | 14.466 | 123.24 | | | |

$\Lambda_0 = 126.42$

TABLE III

EQUIVALENT CONDUCTANCES OF HYDROCHLORIC ACID AT 25°

| Series | $C \times 10^4$ | $\Lambda$ | Series | $C \times 10^4$ | $\Lambda$ |
|---|---|---|---|---|---|
| a | 0.28408 | 425.01 | a | 7.5404 | 421.66 |
| c | 0.81181 | 424.75 | b | 15.768 | 419.88 |
| b | 1.7743 | 423.82 | a | 18.766 | 419.64 |
| a | 3.1863 | 423.43 | c | 25.614 | 418.32 |
| c | 3.4227 | 423.22 | b | 29.943 | 417.98 |
| b | 5.9146 | 422.42 | | | |

$\Lambda_0 = 426.04$

TABLE IV

EQUIVALENT CONDUCTANCES OF POTASSIUM NITRATE AT 25°

| Series | $C \times 10^4$ | $\Lambda$ | Series | $C \times 10^4$ | $\Lambda$ |
|---|---|---|---|---|---|
| a | 0.69820 | 144.17 | b | 12.119 | 141.53 |
| a | 1.7613 | 143.62 | a | 16.468 | 140.91 |
| a | 3.8888 | 142.98 | b | 24.219 | 140.17 |
| b | 5.8651 | 142.61 | b | 36.724 | 139.08 |
| a | 8.6853 | 141.97 | | | |

$\Lambda_0 = 144.92$

TABLE V

EQUIVALENT CONDUCTANCES OF SILVER NITRATE AT 25°

| Series | $C \times 10^4$ | $\Lambda$ | Series | $C \times 10^4$ | $\Lambda$ |
|---|---|---|---|---|---|
| a | 0.27575 | 132.91 | a | 7.5380 | 130.82 |
| b | 0.72453 | 132.64 | b | 10.026 | 130.45 |
| a | 1.0710 | 132.48 | b | 12.297 | 130.10 |
| a | 3.5387 | 131.58 | a | 14.530 | 129.86 |
| b | 4.6704 | 131.46 | b | 29.054 | 128.44 |

$\Lambda_0 = 133.32$

TABLE VI

EQUIVALENT CONDUCTANCES (25°). OBSERVED AND COMPUTED VALUES AT ROUND CONCENTRATIONS

| Concn. | $\Lambda$, KCl Calcd. | Obs. | $\Lambda$, NaCl Calcd. | Obs. | $\Lambda$, HCl Calcd. | Obs. |
|---|---|---|---|---|---|---|
| 0.0001 | 148.89 | 148.90 | 125.54 | 125.56 | 424.46 | 424.53 |
| .0002 | 148.52 | 148.56 | 125.19 | 125.21 | 423.82 | 423.86 |
| .0005 | 147.77 | 147.80 | 124.48 | 124.50 | 422.58 | 422.62 |
| .001 | 146.95 | 146.93 | 123.71 | 123.72 | 421.23 | 421.24 |
| .002 | 145.81 | 145.79 | 122.64 | 122.67 | 419.34 | 419.27 |
| .005 | 143.65 | 143.64 | 120.60 | 120.58 | 415.75 | 415.68 |
| .01 | 141.36 | 141.32 | 118.45 | 118.43 | 411.96 | 411.88 |
| .02 | 138.39 | 138.34 | 115.67 | 115.65 | 407.06 | 407.12 |
| .05 | 133.33 | 133.33 | 110.89 | 110.88 | 398.79 | 398.97 |
| .07 | .... | .... | .... | .... | 395.42 | 395.33 |
| .10 | 128.94 | 128.90 | 106.73 | 106.68 | 391.78 | 391.20 |
| $A$ | $= 0.2274\Lambda_0 + 59.79$ | | 93.85 | 88.53 | | 156.70 |
| $B$ | | | 94.9 | 89.5 | | 165.0 |
| $\Lambda_0$ | | | 149.82 | 126.42 | | 426.04 |

$$\Lambda_0 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} - BC$$

TABLE VII

EQUIVALENT CONDUCTANCES (25°) OF SILVER AND POTASSIUM NITRATES AT ROUND CONCENTRATIONS

| Concn. | $\Lambda$, $AgNO_3$ | $\Lambda$, $KNO_3$ | Concn. | $\Lambda$, $AgNO_3$ | $\Lambda$, $KNO_3$ |
|---|---|---|---|---|---|
| 0.0001 | 132.46 | 144.02 | 0.01 | 124.72 | 135.78 |
| .0002 | 132.08 | 143.53 | .02 | 121.37 | 132.37 |
| .0005 | 131.32 | 142.73 | .05 | 115.20 | 126.27 |
| .001 | 130.47 | 141.80 | .07 | .... | 123.52 |
| .002 | 129.32 | 140.54 | .10 | 109.10 | 120.36 |
| .005 | 127.16 | 138.44 | $\Lambda_0$ | 133.32 | 144.92 |

*in each case, the limiting slope which is approached by the curves representing the actual measurements.*

An empirical extension of Onsager's equation applicable to solutions of strong uni-univalent electrolytes up to about 0.1 normal has been presented in the preceding paper.[23] The equation proposed is

[23] Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} - BC \qquad (5)$$

which differs from Onsager's theoretical limiting equation by the term $BC$. $\Lambda$ is the equivalent conductance, $\Lambda_0$ is the equivalent conductance at infinite dilution, $C$ is the equivalent concentration, $\alpha$ and $\beta$[24] are Onsager's theoretically computed constants depending on the solvent and the temperature, and $B$ is an empirical constant. As has been shown in the preceding paper,[23] Equation 5 is suitable for obtaining $\Lambda_0$ values for hydrochloric acid, potassium chloride and sodium chloride, by applying the equation to the conductivity data with $\Lambda_0$ and $B$ as the adjustable constants.

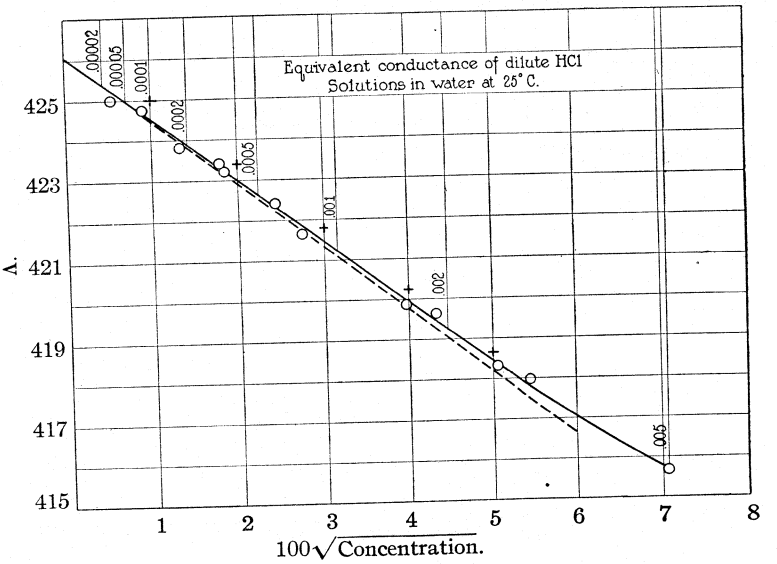


Fig. 6.—○, Shedlovsky; +, Parker.

The limiting values thus obtained agree with the graphical extrapolations, using the measurements on the more dilute solutions in the plots shown in Figs. 5 and 6. The agreement between the observed $\Lambda$ values for hydrochloric acid, potassium chloride and sodium chloride and those calculated from Equation 5 is indicated in Table VI.

The $\Lambda_0$ values for the solutions of potassium nitrate and silver nitrate were obtained by linear extrapolations from the plots of results from the measurements on the most dilute solutions. These plots are shown in Fig. 7. For these substances Equation 5 does not quite fit the observed values. In the case of hydrochloric acid, sodium chloride, and potassium chloride, positive deviations from Onsager's limiting equation, which increase with rising concentration, are observed even below 0.001 normal

[24] At 25° in water $\alpha = 0.2274$; $\beta = 59.79$.

However, in solutions of potassium nitrate and silver nitrate the corresponding deviations have small negative values at first and then become positive, but increase more slowly than is observed for solutions of the chlorides. It therefore appears that a compensating effect is present in these solutions, whose direction is such as might be produced by a slight progressive association of silver nitrate and of potassium nitrate. If this explanation is correct, these salts appear to be somewhat weaker electrolytes than sodium chloride, potassium chloride and hydrochloric acid. However, a more detailed consideration of the conductivity data on silver nitrate and potassium nitrate solutions from this viewpoint will be reserved for a future communication.

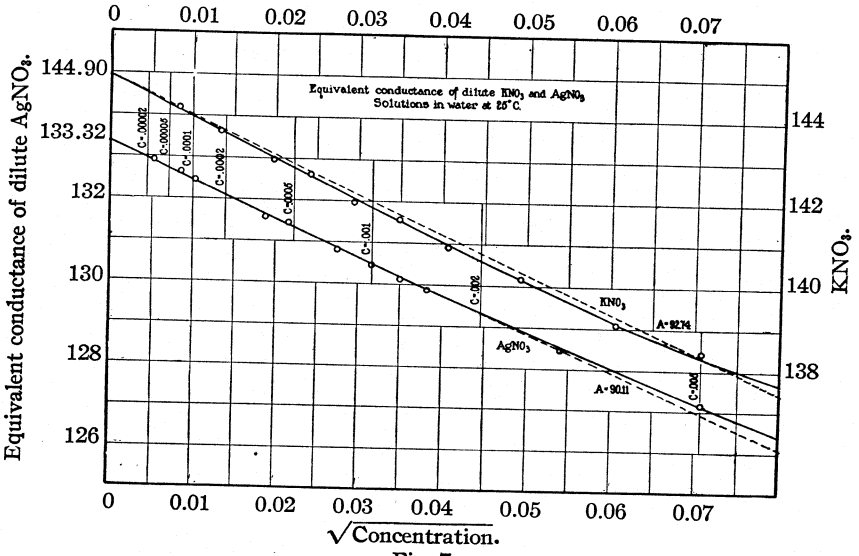


Fig. 7.

In Figs. 5 and 6 some recent measurements at 25° by other workers are compared with my results. The triangles (Fig. 5) indicate conductance values obtained by Grindley and Davies[25] on potassium chloride solutions, and the crosses, values reported by Jeffery and Vogel[26] for potassium chloride and sodium chloride. The crosses (Fig. 6) indicate values obtained by Parker[27] on hydrochloric acid solutions recomputed to the conductance basis of the present measurements. The discrepancies between the new measurements and those of the other workers are probably due, in part at least, to the use of dipping electrodes, whose disadvantage has been discussed in the early part of this paper. In the case of the measurements of

[25] Grindley and Davies, *Trans. Faraday Soc.*, **25**, 129 (1929).
[26] Jeffery and Vogel, *J. Chem. Soc.*, 1715 (1931).
[27] Parker, THIS JOURNAL, **45**, 2017 (1923).

Jeffery and Vogel, there may have been also appreciable earth capacity errors, since these authors apparently did not use an "earth-balancing circuit" in their bridge.

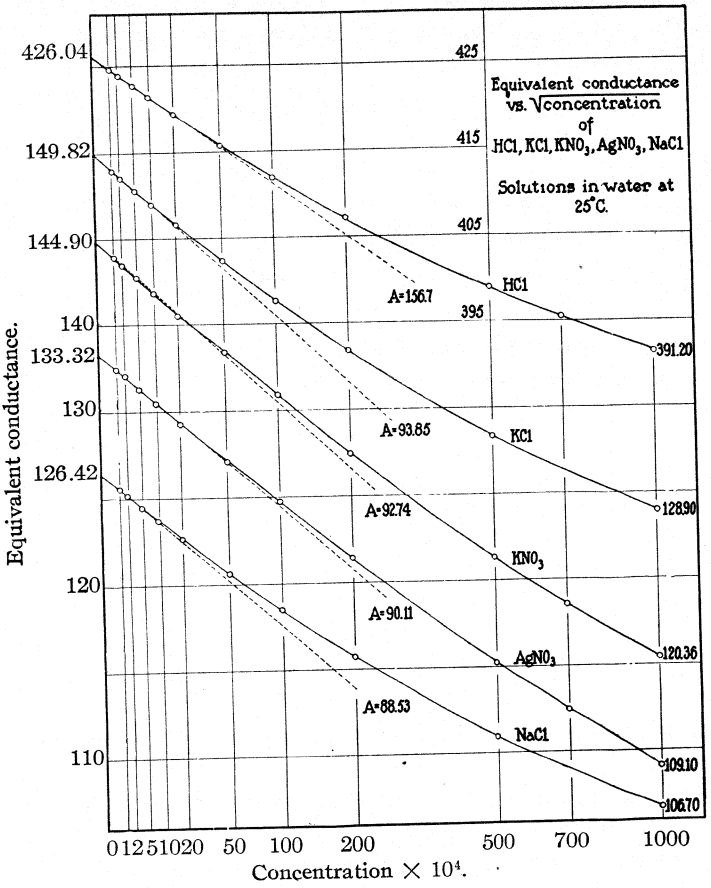


Fig. 8.

**Addendum.**—After this paper had been submitted to THIS JOURNAL, measurements on the conductance of lithium chloride solutions in water at 25° were completed. The results are summarized in the table below. The equivalent conductance of this salt can be represented accurately up to a concentration of 0.07 $N$ by the equation

$$115.00 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} - 89.1\ C$$

The salt was prepared as follows. Lithium carbonate was precipitated from a solution of C. P. lithium chloride with redistilled ammonium carbonate. The carbonate was washed several times with hot water and then

dissolved in distilled hydrochloric acid. The lithium chloride thus formed was crystallized, ignited to remove the volatile impurities, and then recrystallized twice from conductivity water acidulated with pure hydrochloric acid. With the aid of the Richards bottling apparatus the final product was fused in platinum in an atmosphere of dry hydrogen chloride and cooled in vacuum. The product was found to be neutral.

EQUIVALENT CONDUCTANCE OF LITHIUM CHLORIDE AT 25°

| $C$ | $\Lambda$ obs. | $\Lambda$ calcd. | $C$ | $\Lambda$ obs. | $\Lambda$ calcd. |
|---|---|---|---|---|---|
| 0 | .... | 115.00 | 0.032581 | 102.34 | 102.30 |
| 0.00047210 | 113.18 | 113.18 | .009836 | 107.33 | 107.35 |
| .0023455 | 111.04 | 111.05 | .018515 | 104.91 | 104.92 |
| .0058846 | 108.91 | 108.92 | .049942 | 100.10 | 100.06 |
| .0107786 | 107.03 | 107.03 | .064021 | 98.70 | 98.70 |
| .0199375 | 104.64 | 104.61 | .10000 | 95.83 | 96.19 |

The author wishes to express his thanks to Dr. D. A. MacInnes for his kind suggestions in connection with this work.

## Summary

1. The accurate measurement of the conductance of very dilute solutions with a new type of cell is described.

2. It is shown that the use of "dipping electrodes" for accurate conductivity measurements may lead to errors.

3. Measurements of the equivalent conductances of aqueous solutions of sodium chloride, potassium chloride, hydrochloric acid, silver nitrate, and potassium nitrate at 25° are given in the concentration range 0.00003 to 0.1 $N$.

4. These measurements confirm the Onsager conductance equation as a limiting equation.

5. The measurements on the conductances of the chlorides can be expressed, within experimental error, to about 0.1 $N$ by an extension of the Onsager equation containing, besides $\Lambda_0$, only one empirical constant The measurements on solutions of the nitrates, however, show deviations from this equation which may be due to partial association.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

# THE DETERMINATION OF THE IONIZATION CONSTANT OF ACETIC ACID, AT 25°, FROM CONDUCTANCE MEASUREMENTS

BY DUNCAN A. MACINNES AND THEODORE SHEDLOVSKY

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A number of years ago one of the authors published recalculations of the ionization constants of some weak acids, using the most accurate data then available.[1] In these computations, allowance was made for effects due to interionic attractions. These attractions are functions of the ion concentrations and are made evident by their effects on the ion activities and on the ion mobilities.

In the paper mentioned the law of mass action for the ionization of a weak acid was expressed as follows

$$K = \frac{\alpha^2 \gamma_{H^+} \gamma_{A^-} C}{(1 - \alpha)\gamma_{HA}} \qquad (1)$$

in which $K$ is the ionization constant, $\alpha$ is the degree of dissociation, $C$ is the total concentration and $\gamma_{H^+}$, $\gamma_{A^-}$ and $\gamma_{HA}$ are the activity coefficients of the hydrogen ion, the anion and the undissociated acid, respectively.[2]

The effect of interionic attractions on the activity coefficients of ions has been dealt with in the well-known papers of Debye and Hückel. The computation of the degree of dissociation, $\alpha$, from conductance measurements is influenced by interionic forces in that it is necessary to take account of the effect of such forces on the mobilities of the ions. According to the Arrhenius theory, the degree of dissociation $\alpha = \Lambda_c/\Lambda_0$ in which $\Lambda_c$ is the equivalent conductance at the concentration $C$ and $\Lambda_0$ is the equivalent conductance at infinite dilution. This theory involves the assumption that the ion mobilities do not change with the concentration. To show this let $U_c^+$, $U_c^-$, $U_0^+$ and $U_0^-$ be the mobilities of the positive and negative ions at the concentration $C$ and at infinite dilution. Since

$$\Lambda_c = \alpha F(U_c^+ + U_c^-) \qquad (2)$$

and

$$\Lambda_0 = F(U_0^+ + U_0^-) \qquad (3)$$

($\alpha = 1$ in the latter case) then

$$\frac{\Lambda_c}{\Lambda_0} = \frac{\alpha F(U_c^+ + U_c^-)}{F(U_0^+ + U_0^-)} \qquad (4)$$

Thus, $\Lambda_c/\Lambda_0 = \alpha$ only if $U_c^+ + U_c^- = U_0^+ + U_0^-$. This can be true only if the mobilities do not change, or by an improbable compensation.

[1] MacInnes, THIS JOURNAL, **48**, 2068 (1926).

[2] Sherrill and Noyes, *ibid.*, **48**, 1861 (1926), obtained this equation independently and tested it with data on the ionization of the second hydrogen from dibasic acids. See also Davies, *J. Phys. Chem.*, **29**, 977 (1925).

Debye and Hückel[3] and more recently Onsager[4] have shown that changes in ion mobilities with concentration are to be expected, on theoretical grounds, even in very dilute ion solutions. Transference data give conclusive evidence that such changes occur at higher concentrations. The original Arrhenius assumption, *i. e.*, $\alpha = \Lambda_c/\Lambda_0$, is therefore inaccurate at any concentration.

Equation 2 may be used to compute degrees of dissociation if values of the expression $F(U_c^+ + U_c^-)$, which we will call $\Lambda_\epsilon$, are known. Since $\Lambda_c$ is the conductance of a mole of acid, the proportion $\alpha$ of which is in the form of ions, $\Lambda_\epsilon$ is evidently the conductance of a mole of *ions* in a condition in which their mobilities retain the values they have at the concentration $C$. Since we have good evidence that strong electrolytes are completely dissociated, at least in dilute solution, values of $\Lambda_\epsilon$ may be readily found from the following considerations. Let NaAc represent the sodium salt of the weak acid (acetic acid for instance) whose degree of dissociation is desired, then

$$\Lambda_{\epsilon_{HAc}} = \Lambda_{c'_{HCl}} - \Lambda_{c'_{NaCl}} + \Lambda_{c'_{NaAc}}$$

in which the $\Lambda_{c'}$ values are the equivalent conductances of the substances indicated at the ion concentration $C'$. For completely dissociated substances this ion concentration is also the stoichiometric concentration, whereas $\Lambda_{\epsilon_{HAc}}$ is the equivalent conductance of a mole of completely dissociated acetic acid at the *ion* concentration $C'$. Thus for the computation of the degree of dissociation $\alpha = \Lambda_c/\Lambda_\epsilon$ a value of $\Lambda_\epsilon$ must be found which corresponds to the ion concentration of the solution of the weak acid whose measured equivalent conductance is $\Lambda_c$. This involves a short series of approximations. In the previous paper[1] it was shown that for relatively strong acids, such as *o*-nitrobenzoic acid and *o*-chlorobenzoic acid, with ionization constants $6.0 \times 10^{-3}$ and $1.2 \times 10^{-3}$, respectively, true constants for Equation 1 were obtained over the range of concentrations for which data were available. It was, however, rather disturbing to find that the data for the relatively weak acetic acid indicated a definite trend (from $1.74 \times 10^{-5}$ to $1.78 \times 10^{-5}$) of the "constant" in the concentration range 0.07 to 0.002 mole per liter. We felt that it was important to find out whether this drift in the ionization constant was due to inaccuracy of the data available or to the assumptions involved in the computation. In addition, an accurate value of the ionization constant of acetic acid is desirable in other connections. It was decided therefore to obtain, with all possible accuracy, data on the conductance of the acid, and of the other substances (sodium chloride, hydrochloric acid and sodium acetate) involved in the calculation of the ionization constant of this acid.

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

[4] Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

## Experimental

The conductances were determined with the bridge[5] and cells described in a paper from this Laboratory.[6] The data on sodium chloride and hydrochloric acid used in the computations are also reported in the latter paper. The basis for the conductivity values is that a solution containing 7.47896 g. of potassium chloride in 1000 g. of water (weights in air *vs.* brass) has a specific conductance of $0.012852_4$ at 25°.

(a) **Solutions of Acetic Acid.**—C. P. synthetic acetic acid (Niacet Co., U. S. P.) was purified by distilling the material from 2% by weight of potassium permanganate, using an efficient fractionating column.[7] The product was again distilled from a little chromic anhydride. This was followed by a final fractional distillation. Freezing point measurements were made on the separate fractions. After the first quarter of the material was distilled, later fractions, which were kept for use, gave constant freezing points. The purified acid had a freezing point of 16.54° on a thermometer which had been compared with a carefully calibrated platinum resistance thermometer. The specific conductance of the pure acid at 25° was $1.4 \times 10^{-8}$ mhos.

We are indebted to Dr. L. G. Longsworth, of this Laboratory, for a very careful analysis of this acid by the differential potentiometric method recently described.[8] A solution of approximately 0.2 *N* sodium hydroxide used in the titration was calibrated to an accuracy of better than 0.01% against pure benzoic acid from the Bureau of Standards. This solution, which was nearly carbonate free, was kept in large paraffin-lined flasks which were connected with a carbon dioxide absorbing train. By titration of a stock solution, and of small samples of the acid weighed on a micro balance, the purified material was found to be 100.04 ± 0.01% acetic acid. An interesting check on this figure was obtained from the freezing point. Using the cryoscopic constant obtained from De Visser's data[9] and taking Bousfield and Lowry's[7] value of 16.60 ± 0.005° for the freezing point of the pure acid and the freezing point for our acid given above, the value obtained for the strength of the acid is 100.037%, if it is assumed that the freezing point lowering is due to a trace of acetic anhydride.

To prepare the most dilute solutions it was not possible to weigh out small quantities of the glacial acid with sufficient accuracy. It was, therefore, necessary to prepare stock solutions of about 0.1 *N* concentration, weighed increments of which were successively added to the conductivity water in the cell. A difficulty was encountered in dealing with these acetic acid stock solutions. On making titrations on successive days it was found that the acid was growing weaker at the rate of about 0.01% per day. This was not due to attack on the glass wall of the container as a solution of hydrochloric acid showed no such decrease. The effect was finally found to be due to growth of organisms, probably bacteria, in the acetic acid solution. It was overcome, with the kind help of Dr. Alexis Carrel and assistants, by the use of the following sterile technique.

A solution of approximately the concentration desired was made from the pure acid and conductivity water, and was sealed in a half-filled round-bottomed Pyrex flask. This flask was placed in an autoclave at about 15 pounds' steam pressure for an hour or two on three successive days, to make sure that any spores present were killed. The flask was then opened and the solution was transferred to the flask shown in Fig. 1. This flask had also been sterilized. The transfer took place in a chamber

[5] Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).
[6] Shedlovsky, *ibid.*, **54**, 1411 (1932).
[7] Bousfield and Lowry, *J. Chem. Soc.*, **99**, 1432 (1911).
[8] MacInnes and Cowperthwaite, THIS JOURNAL, **53**, 555 (1931).
[9] De Visser, *Rec. trav. chim.*, **12**, 101 (1893).

which had been sprayed free of dust. The flask is similar to that described by MacInnes and Dole[10] with the addition of a close-grained alundum filter, F. With this arrangement the acid can be forced out by a pressure of gas without fear of contamination by bacteria. Acid, in this flask, kept its concentration to within ±0.01% for a month.

The data on the conductance of acetic acid are given in Columns 1 and 3 of Table II. Of these data the measurements of solutions having concentrations below 0.01 *N* were made in the quartz flask cell[6] with a cell constant of 0.58895. Above that concentration the measurements at round values were made in pipet cells,[6] and the others in a Pyrex flask cell with a cell constant of 8.2183.

**(b) Solutions of Sodium Acetate.**—The solutions of dilute sodium acetate cannot readily be prepared to the desired accuracy in the concentrations by weighing out the dry salt or the trihydrate, since neither of these compounds can be obtained with sufficient stoichiometric purity. Also it is necessary to control the hydrolysis of the salt. The following procedure was therefore adopted. Sodium bicarbonate, which can be readily obtained free from the potassium salt and other impurities, was heated in an electric furnace at about 280° to yield sodium carbonate. A stock solution of this material (about 0.1 *N*) was prepared and was titrated electrometrically against standard hydrochloric acid, with an accuracy of about 0.01%. To prepare a solution of sodium acetate from this material, about 1 g. of the glacial acetic acid was weighed out into a quartz ampoule on a micro balance. The necessary amount of the sodium carbonate solution to nearly but not quite neutralize the acid was weighed out into a weighed glass-stoppered flask and the ampoule was dropped into it. The excess of acid was several tenths of a per cent. This flask was then carefully heated to drive off carbon dioxide, which was evolved with practically no spray. After cooling, the flask was again weighed. The concentration of sodium acetate was computed from the known quantity of sodium present. Dilute solutions were prepared by adding small weighed amounts of this stock solution to conductivity water in the cell.

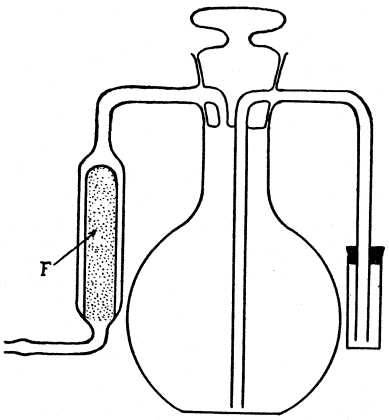

Fig. 1.

A stoichiometric solution of sodium acetate has the disadvantages that it is considerably hydrolyzed and its conductivity is therefore very sensitive to traces of carbon dioxide, since these would react with the liberated hydroxide. The sodium acetate in a solution containing a slight excess of acetic acid is, however, not hydrolyzed and the ionization of carbonic acid is repressed. The solution is, in fact, buffered against these effects. On the other hand, the conductivity of the solutions thus prepared must be corrected for the conductance due to the very slight ionization of the excess acid. This forms a part of the total solvent correction, which includes the conductivity of pure water in the given solution, and a further correction for conductivity due to a trace of neutral salt if the water had been stored in a Vitreosil container. From $P_H$ determinations on the solutions the hydrogen-ion concentration may be computed with sufficient accuracy. This figure and the ion product $(H^+)(OH^-) = K_w$ of water gives the hydroxyl-ion concentration. Since in these measurements the solution was slightly acid, the difference between the hydrogen and hydroxyl concentrations must be balanced by acetate-ion concentration in excess of that arising from the sodium acetate. The

[10] MacInnes and Dole, THIS JOURNAL, 51, 1124 (1929).

magnitude of the correction for the trace of salt was arrived at as follows. The conductivity water from the Vitreosil container also contains a trace of carbonic acid. This was shown in two ways. In the first place, by blowing nitrogen, carefully freed from carbon dioxide, through the water in the conductivity cell the conductance slowly dropped from 3 or 4 $\times 10^{-7}$ to a minimum of about 1.5 to 2 $\times 10^{-7}$. Furthermore, when brom thymol blue, isohydric to $P_H$ 7, was added to a fresh sample of water the color corresponded to about $P_H$ 6.5. However, after the purified nitrogen had been run through the water for about an hour, the color changed to that of $P_H$ 7, and continued passage of gas produced no change. It was thus concluded that the current of gas removed the last traces of carbonic acid and that the minimum conductance measured was due to the pure water plus a minute amount of neutral salt. Since the conductance of pure water at 25° is 0.55 $\times 10^{-7}$, that due to the trace of salt can be found by subtracting this value from the minimum conductance obtained as described above.[11] The complete solvent correction which was applied to the conductivity measurements of the solutions of sodium acetate was a sum of the neutral salt correction to which were added the conductances of hydrogen, hydroxyl and excess acetate ions computed as already described.[12] The $P_H$ value used in these computations was that of the final solution after the concentration had been built up to about 0.005 $N$ by successive additions of the stock solution. This $P_H$ was assumed to be constant throughout the measurements since the mixture is a buffer. Also the 0.005 $N$ solution had very nearly the same $P_H$ as the stock solution, typical values being $P_H$ = 6.60 and $P_H$ = 6.72, respectively. The $P_H$ measurements were made electrometrically in the usual Clark apparatus, by Mr. Donald Belcher.

The conductance data on sodium acetate at 25° are given in Table I, which also includes a comparison of the observed values with those obtained from the equation

$$\Lambda_{NaAc} = 90.97 - 80.48\sqrt{C} + 90C(1 - 0.2274\sqrt{C}) \qquad (5)$$

TABLE I

EQUIVALENT CONDUCTANCES OF SODIUM ACETATE SOLUTIONS AT 25°

| $C \times 10^4$ | $\Lambda$ obs. | $\Lambda$ cal. | $C \times 10^4$ | $\Lambda$ obs. | $\Lambda$ cal. |
|---|---|---|---|---|---|
| 0.99051 | 90.11 | 90.17 | 17.463 | 87.74 | 87.76 |
| 1.8627 | 89.92 | 89.90 | 20.683 | 87.52 | 87.45 |
| 5.9058 | 88.96 | 89.07 | 27.973 | 86.96 | 86.96 |
| 7.3205 | 88.90 | 88.86 | 31.332 | 86.75 | 86.74 |
| 7.6201 | 88.76 | 88.82 | 39.725 | 86.28 | 86.25 |
| 14.237 | 88.03 | 88.06 | 41.243 | 86.16 | 86.17 |
| 15.256 | 87.95 | 87.96 | 43.016 | 86.07 | 86.08 |

[11] The water used in the measurement of the acetic acid solutions was collected directly into the transparent quartz cell. This water had an initial conductivity 1 to 2 $\times 10^{-7}$ *lower* than the water which had been stored in the Vitreosil container. It has been assumed, therefore, that the salt came from the latter container, and consequently no salt correction was required in the case of the acetic acid measurements.

[12] The formula for the total water correction, $L$, for dilute solutions of sodium acetate prepared as described above is

$$L = (L_S + 0.350\ C_{H^+} + 0.196\ C_{OH^-} + 0.041\ C_{Ac^-})$$

in which $L$ is the total correction to the measured specific conductance, $C_{H^+}$ is the hydrogen-ion concentration = $10^{-P_H}$, $C_{OH^-} = 10^{-14}/C_{H^+}$, and $C_{Ac^-} = C_{H^+} - C_{OH^-}$. $L_S$ is the conductance due to neutral salt. The coefficients of the concentration terms are the limiting conductances of the ions times $10^{-3}$.

This equation is of the same form as those used in expressing the conductance of hydrochloric acid and sodium chloride solutions.[6]

## Discussion of Results

As stated in our introduction, the degree of dissociation, $\alpha$, is obtained from the ratio $\Lambda_c/\Lambda_\epsilon$, or, possibly more convenient for computation, the ion concentration $C_i = \alpha C$ may be found from

$$C_i = \frac{1000\,\overline{L}}{\Lambda_\epsilon} \tag{6}$$

in which $\overline{L}$ is the specific conductance of a solution and $\Lambda_\epsilon$ depends upon the ion concentration in the solution. Values of $\Lambda_\epsilon$ (the conductance of completely dissociated acetic acid) as a function of the ion concentration are given by the equation

$$\Lambda_{\epsilon_{HAc}} = 390.59 - 148.61\sqrt{C_i} + 165.5\,C_i(1 - 0.2274\sqrt{C_i}) \tag{7}$$

which was in turn obtained from the equation

$$\Lambda_\epsilon = \Lambda_{HCl} - \Lambda_{NaCl} + \Lambda_{NaAc} \tag{8}$$

in which $\Lambda_{HCl} = 426.04 - 156.70\sqrt{C} + 165.5\,C(1 - 0.2274\sqrt{C})$, $\Lambda_{NaCl} = 126.42 - 88.53\sqrt{C} + 89.5\,C(1 - 0.2274\sqrt{C})$ from the accompanying paper by Shedlovsky[6] and $\Lambda_{NaAc}$ is given by Equation 5 of this communication. This, of course, involves the assumption that Kohlrausch's law of independent ion migration holds at the ion concentrations involved. That no appreciable error arises from this assumption will be shown, from newly obtained data, in a paper to appear shortly from this Laboratory.

To find a value of $\Lambda_\epsilon$ corresponding to an ion concentration $C_i$, involved a short series of approximations. A first approximation was made with the limiting value of $\Lambda_\epsilon$, *i. e.*, $\Lambda_0$, giving $C_i = 1000\,\overline{L}/\Lambda_0$; from this ion concentration a value of $\Lambda_\epsilon$ was found from Equation 7. A new estimate of $C_i$ was then made, followed by another of $\Lambda_\epsilon$, until repetition did not change the result. Usually three approximations were sufficient. From the resulting $C_i$ values a series of values of

$$K' = \frac{\alpha^2 C}{1 - \alpha} = \frac{C_i^2}{(C - C_i)} \tag{9}$$

were obtained. These are given in Column 5 of Table II. It will be recalled that $K'$ is the mass action "constant" uncorrected for changes in activity coefficients.

From Equation 1 it may be seen that the thermodynamic ionization constant $K$ is related to $K'$ by

$$K = K'\frac{\gamma_i^2}{\gamma_u} \tag{10}$$

TABLE II

EQUIVALENT CONDUCTANCES AND IONIZATION CONSTANT VALUES OF ACETIC ACID AT 25°

| Total concn. $C \times 10^3$ | Ion concn. $C_i \times 10^4$ | $\Lambda_c$ | $\Lambda_0$ | $K' \times 10^5$ | $K \times 10^5$ |
|---|---|---|---|---|---|
| 0.028014 | 0.15107 | 390.02 | 210.32 | $1.768^2$ | $1.752^2$ |
| .11135 | .36491 | 389.68 | 127.71 | $1.778^7$ | $1.753^8$ |
| .15321 | .44049 | 389.61 | 112.02 | $1.777^5$ | $1.750^2$ |
| .21844 | .54101 | 389.49 | 96.466 | $1.781^0$ | $1.750^7$ |
| 1.02831 | 1.2727 | 388.94 | 48.133 | $1.797^4$ | $1.750^8$ |
| 1.36340 | 1.4803 | 388.81 | 42.215 | $1.803^0$ | $1.752^6$ |
| 2.41400 | 2.0012 | 388.52 | 32.208 | $1.809^0$ | $1.750^3$ |
| 3.44065 | 2.4092 | 388.32 | 27.191 | $1.814^0$ | $1.749^6$ |
| 5.91153 | 3.1929 | 387.99 | 20.956 | $1.823^0$ | $1.748^7$ |
| 9.8421 | 4.1557 | 387.61 | 16.367 | $1.832^0$ | $1.746^9$ |
| 12.829 | 4.7591 | 387.41 | 14.371 | 1.834 | 1.743 |
| 20.000 | 5.975 | 387.05 | 11.563 | 1.840 | 1.738 |
| 50.000 | 9.524 | 386.19 | 7.356 | 1.849 | 1.721 |
| 52.303 | 9.7542 | 386.07 | 7.200 | 1.854 | 1.723 |
| 100.000 | 13.496 | 385.29 | 5.200 | 1.846 | 1.695 |
| 119.447 | 14.763 | 385.07 | 4.759 | 1.847 | 1.689 |
| 200.000 | 18.992 | 384.41 | 3.650 | 1.821 | 1.645 |
| 230.785 | 20.371 | 384.15 | 3.391 | 1.814 | 1.633 |

in which $\gamma_i$ is the mean activity coefficient of the ions and $\gamma_u$ that of the undissociated acid. Thus

$$\log K = \log K' + 2 \log \gamma_i - \log \gamma_u \qquad (11)$$

However, from the Debye–Hückel theory in its limiting form

$$- \log \gamma_i = 0.5065 \sqrt{C_i} \qquad (12)$$

and also in the limit $\gamma_u = 1$. Thus

$$\log K = \log K' - 1.013 \sqrt{C_i} \qquad (13)$$

This limiting equation accounts with surprising accuracy for the measurements at the five or six lowest concentrations, as is shown in Fig. 2, in which the logarithms of $K'$ are plotted against the square roots of the corresponding ion concentrations. In this plot the solid line $e$ has the theoretical slope 1.013 of Equation 13. The excellent agreement between the theory and the experimental results for the more dilute solutions is also shown in Column 6 of Table II, in which the values of the thermodynamic constant $K$ computed from Equation 13 are listed. For the lower range of concentrations these vary but slightly from a mean of $1.752 \times 10^{-5}$.[13] Above an acid concentration of about 0.01 $N$ the computed values of the ionization constant decrease.

There are a number of reasons why this should be the case. In the first place we have used the limiting form of the Debye–Hückel equation

[13] In our recent "Letter to the Editor," THIS JOURNAL, 53, 2419 (1931), the slightly lower values of $K$ resulted from calculations made before our complete data on the conductivity of hydrochloric acid were available.

for computing the activity coefficients of the ions. If account is taken of the size of the ions, instead of Equation 13 we have

$$-\log \gamma = 0.5065 \frac{\sqrt{C}}{1 + 0.327\ a\sqrt{C}} \qquad (14)$$

(where $a$ is the distance of closest approach of ions in Ångström units). This equation is valid for the ion concentrations involved in our computations if $a$ is greater than 3 Å.[14] In the second place the assumption that the activity coefficient of the undissociated acid $\gamma_u$ is unity is true only at sufficiently low concentrations. The correction for this deviation is relatively small. It can be evaluated, however, from freezing point

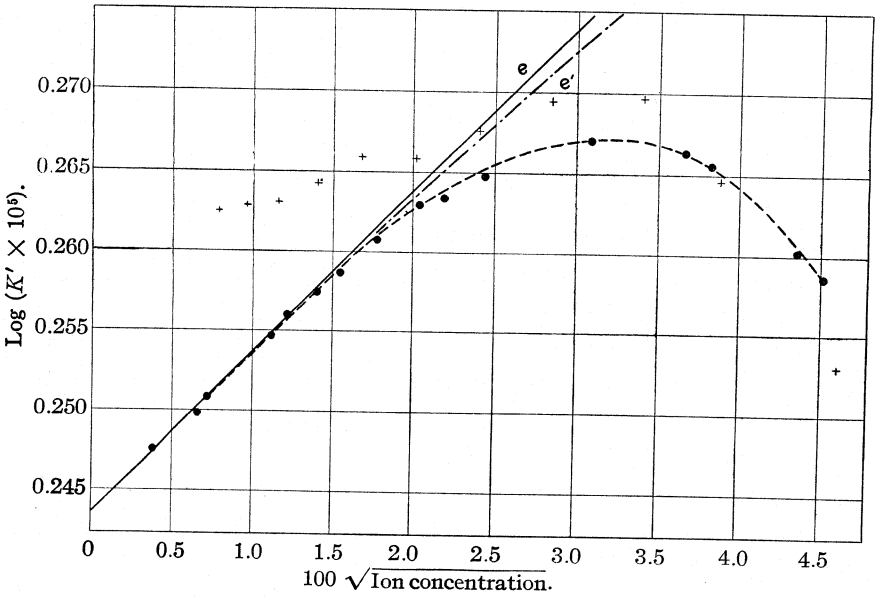


Fig. 2.—●, MacInnes and Shedlovsky; +, Kendall.

measurements, as has been shown by Lewis and Randall.[15] Although both of these effects are in the right direction, they are not nearly large enough to account for the observed deviations. This is shown in Fig. 2 where the broken line $e'$ represents the variation of $K'$ which would be expected if the activity coefficients were modified to allow for the two foregoing effects. In this calculation it has been assumed that $a$ is of the order of 4 Ångström units, as can be roughly estimated from crystal structure data. It will be observed that the effects of ion size and activity coef-

[14] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928), give a further extension of the theory which must be used for small ions or higher valences.

[15] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, pp. 284, 290.

ficients of the undissociated material are not sufficient to account for the variation of $K'$ observed.[16]

In computing $K$ it has been assumed that the accumulation of undissociated acetic acid with increasing concentration has no effect on the solvent. The properties of undissociated acetic acid are, however, quite different from those of water. For instance, the acid has a low dielectric constant, less than 10 per cent. of that of water, and its presence in undissociated form in the aqueous solutions would be expected to influence the *mobilities* as well as the activities of the ions. In our computation it has been necessary, with the data at hand, to assume that the solvent is pure water. This is evidently incorrect at the higher concentrations, and will lead to greater errors the weaker the electrolyte. We expect, in the near future, to study the effect of the change of the medium on the mobilities of the ions.[17]

Referring to Fig. 2 it is seen that line *e*, as has been mentioned, represents the Debye–Hückel theoretical limiting slope, *i. e.*, the constant $2A = 1.013$ in the expression $-\log \gamma_i^2 = 2A\sqrt{C_i}$. Although this line is evidently in close agreement with the data for the lower concentrations, it is nevertheless a limiting equation, and deviations from it must be considered for obtaining the most probable value of the constant $K$ from the

[16] The change of the activity of the solvent must also be considered at higher concentrations since the ionization in its simplest terms is

$$HAc + H_2O = H_3O^+ + Ac^-$$

Also see Kendall, THIS JOURNAL, **39**, 2323 (1917).

[17] Davies [*Phil. Mag.*, **4**, 244 (1927)] finds that a constant can be obtained from Kendall's conductance data on acetic acid if the conductances are multiplied by the viscosity at each concentration. However, he obtains a higher value than we do for the constant; furthermore, he uses an empirical value of $A = 0.393$ in the limiting equation $-\log \gamma = A\sqrt{C}$ instead of the theoretical value $A = 0.5065$ obtained by Debye and Hückel. He considers that this observation supports Milner's theory (which leads to a lower value of $A$) rather than the Debye–Hückel theory, and also that it sustains Nonhebel's experimental value of $A = 0.39$ obtained from e. m. f. data [Nonhebel, *Phil. Mag.*, **7**, ii, 1085 (1926)]. Kendall's data may be readily shown to be of insufficient accuracy to decide the question. In Fig. 2 values of $K'$, which have been calculated from Kendall's data, are compared with our results. In these computations his conductances for acetic acid have been reduced to our basis and our data for the other electrolytes have been used. It will be seen that there is a progressive deviation of these values of $K'$ from ours as the concentrations decrease. This is what would be expected from Kendall's procedure. His measurements on the more concentrated solutions were made first and the concentrations successively reduced by halves, the dilutions being carried out in air in a glass conductivity cell. The most dilute solution thus had the most handling and had the greatest contamination. Also any adsorption of the acid from the concentrated solutions would likewise tend to contaminate the dilute solutions. The apparent need for a viscosity correction to the data, for the more dilute solutions at least, thus arose from experimental error. As Davies has observed, there is no need for such a correction to the data for the stronger acids.

data. Accordingly least square computations were made on the eight and ten lowest points, using the equation

$$\log K' = \log K - 2A\sqrt{C_i} + BC_i$$

The results are given below

| | $2A$ | $B$ | $K \times 10^5$ |
|---|---|---|---|
| 8 lowest points | 0.9946 | −0.023 | 1.7533 |
| 10 lowest points | 1.041 | −0.047 | 1.7526 |

Although the computed values of 2 $A$ are, respectively, 2% below and 3% above the theoretical value 1.013, the corresponding variations in the activity coefficients, in the ion concentration range of these measurements, are of the order of a few hundredths of a per cent. Thus the values of 2 $A$ are in complete agreement with the theory within the precision of the measurements.

These least square computations give us the limiting value of $K' = 1.753 \times 10^{-5}$, which is also the result obtained in extrapolating from a plot of the $K$ values in Table II against $C_i$. These constants agree excellently with the value $1.75 \times 10^{-5}$ obtained in a very different manner (from e. m. f. measurements on cells without liquid junction) by Harned and Owen.[18]

## Summary

Conductance measurements at 25° are reported on aqueous solutions of acetic acid in the concentration range 0.00003 $N$ to 0.2 $N$, and on solutions of sodium acetate (in which hydrolysis has been repressed) in the range 0.0001 to 0.004 $N$.

With these data and measurements of hydrochloric acid and sodium chloride, given in an accompanying paper, values of the stoichiometric ionization constants ($K'$) of acetic acid at 25° have been computed. In this computation it has been assumed that the strong electrolytes are completely dissociated and that, for the low ion concentrations involved, the Kohlrausch law of independent ionic mobilities holds. At high dilutions the relation between $K'$ and the true (thermodynamic) ionization constant $K$, *i. e.*, $K = K'\gamma_i^2$ (in which $\gamma_i$ is the mean ionic activity coefficient) is confirmed if values of $\gamma_i$ are calculated from the Debye–Hückel theory. In fact the data corresponding to solutions of acetic acid below 0.01 $N$ are in quantitative agreement with the theory. Above that concentration a strong "medium effect," which probably has its greatest influence on ionic mobilities, becomes apparent.

From the measurements at the higher dilutions the value obtained for the thermodynamic ionization constant $K$ is $1.753 \times 10^{-5}$, which is in excellent accord with recent determinations by electromotive force methods.

NEW YORK, N. Y.

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

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

# THE ACTIVITY COEFFICIENT OF BARIUM HYDROXIDE IN AQUEOUS SOLUTION AT 25°

BY HERBERT S. HARNED AND C. MORGAN MASON[1]

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The present communication is concerned with the calculation of the activity coefficient of barium hydroxide in aqueous solution at 25° through the concentration range of 0 to the saturated solution from electromotive force measurements of the cells.

$$H_2 \mid Ba(OH)_2\ (m) \mid Ba_xHg \mid Ba(OH)_2\ (m_0) \mid H_2$$

## Materials and Experimental Procedure

The concentrated barium hydroxide solutions made from a high grade analyzed chemical were allowed to stand for a week until all carbonate had settled. The clear solutions were carefully drawn off and kept in bottles containing carbon dioxide-free air. The concentrations were determined by titration with hydrochloric acid standardized by gravimetric analysis. Weight burets were employed. Dilute solutions were prepared by addition of known weights of boiled water *in vacuo*. Since measurements of cells of this type are among those most difficultly reproducible, the sources of error lie in the operation of the cells and not in the knowledge of the concentrations of the solutions.

A 0.2% barium amalgam was made by electrolysis of a saturated solution of barium hydroxide. This was withdrawn into an evacuated flask which was then inverted and allowed to stand for twenty-four hours or more until all the usual solid impurities had risen to the surface. This amalgam was then diluted to 0.1% by withdrawal into an equal volume of mercury in a similar vessel.

The cells were similar in design to those previously described by Harned[2] and by Åkerlöf[3] with one modification. It was found by Lucasse[4] that alkaline earth metal amalgams which flowed from the ordinary type of drawn capillary tubes did not function well in cells of this type. He found that amalgam vessels with turned up capillaries which had not been drawn to fine tips functioned in a much more satisfactory manner. Our experience confirmed this point, so that this type of amalgam vessel was employed.

All solutions were boiled *in vacuo* to remove dissolved air, and all pre-

[1] The present communication was constructed from part of a Dissertation to be submitted to the Graduate School of Yale University in partial fulfilment of the Degree of Doctor of Philosophy, June, 1932.

[2] Harned, THIS JOURNAL, **47**, 676 (1925).

[3] Åkerlöf, *ibid.*, **48**, 1160 (1926); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[4] Lucasse, THIS JOURNAL, **47**, 743 (1925).

cautions accompanying the manipulation of cells of this type were observed. The measurements were made at 25 ± 0.02°.

It should be mentioned that these cells are among the most difficult to manipulate. Very small quantities of dissolved air caused large errors. The average error in reproducibility is estimated to be ±0.3 mv. Therefore, we have relied on a large number of measurements in order to minimize the accidental variations.

## Method of Calculation and Results

The electromotive force of the cell

$$H_2 \mid M(OH)_2\ (m) \mid M_xHg \mid M(OH)_2\ (m_0) \mid H_2$$

is given by the equation

$$E = 0.08873 \log \frac{\gamma m}{\gamma_0 m_0} + 0.05915 \log \frac{a_{H_2O(m_0)}}{a_{H_2O(m_0)}} \qquad (1)$$

In general, it is necessary to know the activity of water in the hydroxide solution in order to obtain $\gamma$. As shown by Harned,[2,5] the second term on the right of equation (1) may be evaluated from the electromotive forces by an arithmetical calculation. This procedure was adopted for the cells containing barium hydroxide and it was found that the numerical value of this term was less than the experimental error in the determination of $E$ throughout the moderate concentration range of 0 to 0.23 molal. Indeed, this factor does not exceed 0.1 mv.

Table I contains the measurements. $m$ is the molality, $c$ the concentration in moles per liter of solution, $d$ the density of the solution determined for the purposes of the calculations to follow, and $E$ the observed electromotive forces of the cell containing 0.12 $M$ barium hydroxide as the reference solution, so that $m_0$ always equaled 0.12 $M$. The sixth column contains the number of cells measured at each molality and the seventh column contains the total deviation in millivolts of these measurements. In order to render the results more consistent, $E$ was plotted against log $m$, and the smoothed out results given in the fifth column were read off the plot.

The values of the activity coefficients were obtained by employing Hückel's equation

$$\log \gamma = -\frac{0.708\sqrt{6c}}{1 + A\sqrt{6c}} + B(6c) - \log(1 + 0.054m) \qquad (2)$$

where $A$ and $B$ are constants. In order to evaluate $A$ and $B$, three electromotive forces are necessary, and these were read off the curve at 0.01, 0.06, and 0.12 molal. Since the method of obtaining $A$ and $B$ from cells of this type has been previously described,[6] we shall not discuss the matter further. $A$ and $B$ were found to be 0.696 and 0.0113, respectively. The eighth column of the table contains the values of $\gamma$ computed by equation

[5] Harned and Schupp, THIS JOURNAL, **52**, 3886 (1930).

[6] Hückel, *Physik. Z.*, **26**, 93 (1925); Harned, THIS JOURNAL, **48**, 326 (1926).

TABLE I

ACTIVITY COEFFICIENTS OF BARIUM HYDROXIDE IN AQUEOUS SOLUTIONS AT 25° FROM MEASUREMENTS OF CELLS

$H_2 \mid Ba(OH)_2\ (m) \mid Ba_xHg \mid Ba(OH)_2\ (0.12) \mid H_2$

| $m$ | $c$ | $d$ | $E$ (obs.) | $E$ (curve) | No. of cells | Deviation, mv. | $\gamma$ (Hückel) | $\gamma$ (obs.) | $\gamma$ (curve) |
|---|---|---|---|---|---|---|---|---|---|
| 0.0 | .... | 0.9970 | ..... | ..... | . | ... | .. | .. | .. |
| .00245 | 0.002445 | .9977 | −0.1245 | −0.1238 | 2 | 0 1 | 0.834 | 0.820 | 0.835 |
| .00390 | .00389 | .99795 | − .1078 | − .1078 | 1 | .0 | .799 | .795 | .795 |
| .00409 | .00408 | .9980 | − .1069 | − .1062 | 2 | .4 | .795 | .776 | .790 |
| .00500 | .00499 | .99815 | − .0976 | − .0993 | 2 | .2 | .780 | .808 | .773 |
| .00603 | .00601 | .99835 | − .0928 | − .0927 | 1 | ... | .761 | .760 | .761 |
| .00621 | .00619 | .9984 | − .0922 | − .0918 | 2 | .7 | .759 | .749 | .757 |
| .00793 | .00790 | .9987 | − .0840 | − .0836 | 2 | .5 | .735 | .726 | .733 |
| .00991 | .00988 | .9991 | − .0762 | − .0761 | 3 | .2 | .713 | .711 | .713 |
| .01 | .009974 | .9991 | ..... | − .0758 | . | ... | (.712) | .. | (.712) |
| .01132 | .01129 | 0.9993 | − .0725 | − .0718 | 2 | .2 | .699 | .685 | .697 |
| .01509 | .01505 | 1.0000 | − .0630 | − .0628 | 2 | .3 | .668 | .657 | .661 |
| .01577 | .01573 | 1.0002 | − .6020 | − .0614 | 2 | 1.0 | .663 | .647 | .658 |
| .02015 | .02010 | 1.0010 | − .0540 | − .0537 | 2 | 0.3 | .635 | .622 | .627 |
| .02037 | .02030 | 1.0010 | − .0537 | − .0533 | 1 | ... | .634 | .620 | .626 |
| .02045 | .02040 | 1.0011 | − .0523 | − .0532 | 2 | .7 | .633 | .640 | .623 |
| .02050 | .02045 | 1.0011 | − .0528 | − .0531 | 2 | .8 | .633 | .631 | .623 |
| .03077 | .03070 | 1.0029 | − .0397 | − .0404 | 2 | .5 | .585 | .580 | .579 |
| .03089 | .03082 | 1.0029 | − .0399 | − .0402 | 2 | .7 | .585 | .576 | .580 |
| .03915 | .03906 | 1.0045 | − .0327 | − .0329 | 2 | .7 | .556 | .558 | .553 |
| .04083 | .04074 | 1.0048 | − .0314 | − .0316 | 2 | .2 | .552 | .552 | .549 |
| .04970 | .04960 | 1.0065 | − .0254 | − .0256 | 2 | 1.5 | .528 | .531 | .527 |
| .05000 | .04990 | 1.0065 | ..... | − .0254 | . | ... | (.527) | .. | (.526) |
| .05323 | .05312 | 1.0071 | − .0233 | − .0234 | 2 | 0.9 | .519 | .522 | .521 |
| .06000 | .05988 | 1.0083 | ..... | − .0200 | . | ... | (.505) | .. | (.505) |
| .06150 | .06140 | 1.0086 | − .0197 | − .0193 | 1 | ... | .502 | .496 | .501 |
| .06162 | .06151 | 1.0087 | − .0191 | − .0192 | 2 | .1 | .502 | .503 | .502 |
| .06210 | .06198 | 1.0087 | − .0187 | − .0189 | 2 | .0 | .501 | .504 | .502 |
| .07152 | .07140 | 1.0105 | − .0151 | − .0149 | 2 | .3 | .484 | .481 | .483 |
| .07983 | .07970 | 1.0120 | − .0121 | − .0118 | 2 | .9 | .471 | .465 | .469 |
| .08015 | .08002 | 1.0121 | − .0117 | − .0117 | 1 | ... | .471 | .469 | .469 |
| .08154 | .08141 | 1.0123 | − .0111 | − .0111 | 2 | .8 | .469 | .468 | .468 |
| .09167 | .09153 | 1.0142 | − .0072 | − .0078 | 1 | ... | .455 | .460 | .453 |
| .09764 | .09750 | 1.0153 | − .0057 | − .0060 | 2 | .1 | .448 | .452 | .446 |
| .1055 | .1054 | 1.0168 | − .0036 | − .0038 | 2 | 1.1 | .439 | .445 | .437 |
| .1200 | .1199 | 1.0194 | ..... | .0000 | . | ... | (.424) | (.424) | (.424) |
| .1476 | .1475 | 1.0246 | + .0060 | + .0060 | 2 | 0.5 | .402 | .402 | .402 |
| .1781 | .1780 | 1.0303 | + .0112 | + .0112 | 2 | .3 | .382 | .382 | .382 |
| .1890 | .1890 | 1.0322 | + .0133 | + .0130 | 1 | ... | .376 | .380 | .377 |
| .1996 | .1996 | 1.0346 | + .0144 | + .0144 | 2 | .2 | .371 | .370 | .370 |
| .2296 | .2296 | 1.0397 | + .0185 | + .0185 | 2 | .1 | .357 | .358 | .358 |

(2), the ninth column contains the values computed by equation (1) by employing the value at $m_0$ equals 0.1200 of 0.424 computed by equation

(2), and the tenth column similar values computed from the smoothed results.

The agreement of the smoothed out values with those computed by the equation is good. All three series of $\gamma$ values agree well in the more concentrated solutions. In the dilute solutions, the behavior of the directly observed values in column (9) is somewhat erratic.

## Summary

1. Measurements of the cells

$$H_2 \mid Ba(OH)_2\ (m) \mid Ba_xHg \mid Ba(OH)_2\ (0.12M) \mid H_2$$

through a concentration range from 0.002 to 0.23 $M$ at 25° have been made.

2. The densities, $d_{25}$, of aqueous barium hydroxide solutions at 25° have been determined and are given to within ± 1 in the fourth decimal place by the equation

$$d_{25} = 0.9970 + 0.1878m$$

3. The activity coefficient of barium hydroxide in aqueous solution has been evaluated by employing Hückel's equation, which upon substitution of the numerical values of the constants $A$ and $B$ becomes

$$\log \gamma = -\frac{0.708\sqrt{6c}}{1 + 0.696\sqrt{6c}} + 0.0678c - \log(1 + 0.054m)$$

NEW HAVEN, CONNECTICUT

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

# THE HEATS OF SOLUTION OF GASEOUS METHYLAMINE

BY W. A. FELSING AND P. H. WOHLFORD

RECEIVED DECEMBER 17, 1931 PUBLISHED APRIL 6, 1932

**Object of the Investigation.**—In a previous paper[1] there were presented some preliminary values for the total heats of solution of gaseous monomethylamine in water at different concentrations of methylamine produced. These preliminary data were included at that time to give an idea of the order of magnitude of this heat effect and to present a more complete listing of the thermodynamic properties of methylamine with the view of using this substance as a refrigerating fluid. Since the appearance of that paper, more reliable data have been obtained; these are presented in the present paper.

**Existing Data.**—Besides the preliminary data of Felsing and Thomas, there are listed but few determinations or calculations of this heat effect in the literature. Bonnefoi[2] presents two experimental values and Moore and Winmill[3] present a calculated value; the values given by Bonnefoi are 11,780 and 12,400 cal./mole of methylamine when the ratio of moles of

[1] Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

[2] Bonnefoi, *Ann. chim. phys.*, **23**, 362 (1905).

[3] Moore and Winmill, *J. Chem. Soc.*, **101**, 1667 (1912)

water to moles of methylamine in the solutions formed are, respectively, 588.4 and 606.8.

## Experimental Procedure

The total heat of solution of gaseous methylamine in water was measured by passing the dry gas into distilled water, observing the temperature rise, and determining the concentration of the methylamine solution produced.

The method used was essentially that employed by Felsing and Stiles[4] in obtaining the heats of solution of sulfur dioxide. The exact arrangement of the apparatus is shown in the figure. The details of manipulation, in general, are identical with those of Felsing and Stiles.

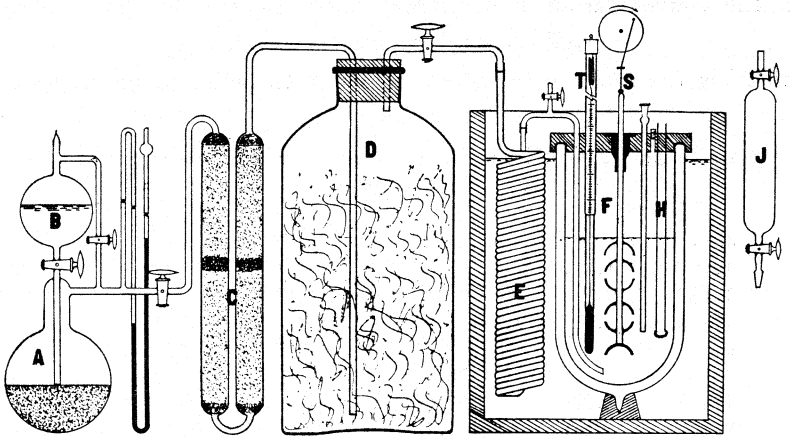


Fig. 1.

A is a generator filled with methylamine hydrochloride (free from ammonium chloride and trimethyltrimethylenetriamine); B is a reservoir of concentrated potassium hydroxide; C is a drying system containing fused barium oxide and flake sodium hydroxide; D is a large bottle filled loosely with metallic sodium ribbon; E is a coil of 6.6-mm. copper tubing about 15 meters long; and F is the calorimeter. A highly evacuated silvered Dewar flask contains a calibrated 2° Beckmann thermometer T, a motor-driven glass stirrer S, a heating element H (61 cm. of No. 24 B. and S. platinum wire, in coil form, soldered to heavy copper leads), and a weight buret sampler. The coil and the calorimeter are immersed in an accurately controlled thermostat kept at 35°.

The *water equivalent* of the calorimeter, determined in the usual manner with all precautions, was found to be 21.7 cal./deg.; the maximum deviation of six determinations was 1.1 calories.

No radiation corrections were applied in the heat of solution determinations since (1) the Dewar flask was highly evacuated and silvered, (2) the stirring rate was held constant throughout, (3) the surroundings were kept at constant temperature and (4) the time of calibration (the water equivalent determinations) was made, by trial, the same in length at the time of an actual heat of solution determination. Only traces of methylamine gas escaped absorption.

[4] Felsing and Stiles, THIS JOURNAL, **48**, 1543 (1926).

The dry methylamine gas was passed from the storage reservoir D into the calorimeter, where it was absorbed by a weighed quantity of distilled water. The temperature rise was noted and a 50-cc. sample of the resulting solution was removed by means of the sampling pipet J. A weighed quantity of solution was titrated against standard sulfuric acid, using methyl red as an indicator. All titrations and standardizations were made by weight; the usual precautions for highest accuracy were observed carefully and duplicate determinations were always made.

**Data.**—The data are listed in Table I; the order of presentation is made identical with the decreasing concentration of methylamine solution produced. It is not the order of actual determination. The functional relation which expresses the dependence of the total heat of solution upon the concentration of solution formed is given by the equation

$$-\Delta H(\text{cal./mole}) = 10{,}627 + 0.24193\ N \qquad (1)$$

where $N$ is the ratio of the moles of water to moles of methylamine.

TABLE I

OBSERVED AND CALCULATED VALUES OF THE TOTAL HEATS OF SOLUTION OF METHYLAMINE

| No. | $\Delta t$(°C.) | $CH_3NH_2$, g. | $H_2O$, g. | $N$ (moles $H_2O$/ moles $CH_3NH_2$) | $-\Delta H$(calcd./mole) Observed | Calcd. by Eq. (1) |
|---|---|---|---|---|---|---|
| 1 | 1.822 | 1.1650 | 197.55 | 292.2 | 10,649 | 10,698 |
| 2 | 1.588 | 0.8894 | 171.54 | 332.3 | 10,704 | 10,707 |
| 3 | 1.469 | .8670 | 182.02 | 361.7 | 10,717 | 10,714 |
| 4 | 1.281 | .7039 | 168.11 | 411.5 | 10,725 | 10,727 |
| 5 | 1.263 | .7389 | 179.65 | 418.9 | 10,689 | 10,728 |
| 6 | 1.129 | .6149 | 166.68 | 467.0 | 10,741 | 10,740 |
| 7 | 0.808 | .5101 | 197.45 | 666.9 | 10,780 | 10,788 |
| 8 | .728 | .3948 | 167.12 | 729.3 | 10,810 | 10,803 |
| 9[a] | .667 | .3762 | 174.80 | 800.1 | 10,814 | 10,821 |
| 10 | .618 | .3449 | 170.90 | 853.7 | 10,815 | 10,834 |
| 11[a] | .574 | .3400 | 185.50 | 940.0 | 10,857 | 10,854 |
| 12 | .518 | .3190 | 194.07 | 1048.1 | 10,881 | 10,881 |

[a] Data by W. W. Floyd.

The variation of the total heat of solution per mole with the concentration of methylamine produced, at any concentration, is given by

$$d(-\Delta H)/dN = 0.24193 \qquad (2)$$

Bonnefoi, on diluting a methylamine solution containing 1 mole in 2 liters with 4 parts of water, obtained a value of 40 cal. per mole as the *heat of dilution*. The corresponding values of $N$ are approximately 111 and 555. Integrating Equation 2 between these limits there results a value of 107.3 calories as the heat of dilution, which value is to be compared with Bonnefoi's value of 40 calories.

## Summary

1. The total heat of solution of gaseous monomethylamine has been determined at 35° for various concentrations of methylamine produced.

2. The relation between $-\Delta H$ (cal./mole of methylamine) and $N$ (moles of water/moles of methylamine) is given by the linear equation $-\Delta H = 10{,}627 + 0.24193\ N$; the experimental values agree with the values calculated by this relation on the average to within 0.11%; the maximum deviation is 0.46%.

AUSTIN, TEXAS

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## NOTE

### Note on the Preparation of Absolute Isopropanol

BY LEWIS E. GILSON

During several years of biochemical research the writer has found many instances where isopropanol could be substituted for ethanol in laboratory work. It is cheap and there are no restrictions governing its use; nor is it likely to be an object of theft. The commercial 91% azeotropic mixture was used instead of 95% ethanol and found to be fully equal or superior to the latter as a solvent or extracting medium. Absolute isopropanol was used in place of absolute ethanol.

Absolute isopropanol is easily prepared. The 91% grade is shaken with 10% of its weight of commercial flake sodium hydroxide, separated from the aqueous layer which forms, then shaken with a little more sodium hydroxide, decanted and distilled. The product obtained mixes with eight volumes of carbon disulfide, xylene or petroleum ether without the slightest trace of turbidity.

Dilute isopropanol can be concentrated by shaking with dry sodium chloride. Water is removed as a saturated layer of brine. The upper layer contains about 87% isopropanol and 2–3% of sodium chloride. While distilling, an additional quantity of brine separates. The distillate has so nearly the composition of the 91% azeotropic mixture that it can be used as such without further treatment. Or, after shaking the dilute isopropanol with sodium chloride and separating, it can be treated directly with sodium hydroxide and the absolute grade prepared.

CONTRIBUTION FROM THE
BIOCHEMISTRY DEPARTMENT
UNIVERSITY OF CINCINNATI
CINCINNATI, OHIO

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

# A NEW METHOD FOR THE PREPARATION OF DIARYLPHTHALIDES[1]

BY F. F. BLICKE AND O. J. WEINKAUFF

RECEIVED AUGUST 22, 1931 PUBLISHED APRIL 6, 1932

During a study of synthetic laxatives it became necessary to obtain a supply of phenolphthalein (4′,4″-dihydroxydiphenylphthalide) entirely free from the by-products which result during the manufacture of this substance. Certain of these by-products—presumably some type of anthraquinone—are extremely potent cathartics and yellow phenolphthalein, that is, phenolphthalein which has not been subjected to a thorough purification process and which is contaminated with a small quantity of a yellow, alkali-soluble, resinous material, is used extensively as a laxative.[2]

Furthermore, we wished to obtain a sample of isophenolphthalein (2′,4″-dihydroxydiphenylphthalide) in order that its physiological properties might be reinvestigated. In a preliminary report by Hatcher[3] it is recorded that isophenolphthalein exhibits no cathartic action on humans. In view of the fact that this substance differs from phenolphthalein only in the respect that it is a 2′,4″-dihydroxy instead of a 4′,4″-dihydroxy derivative, it would be conceivable that the material might be less active than phenolphthalein but it seemed very strange that the compound should have been found to be entirely inert. Although our tests were carried out only on a very limited scale, the results obtained with the isophenolphthalein prepared by us agreed with those of Hatcher. Administered, mixed with milk sugar, in the form of gelatine capsules, no laxative effect was obtained with human subjects even with doses as large as four grains.

One of the objectionable features of many of the syntheses described hitherto is that in addition to the desired phthalide, by-products such as isomeric phthalides or anthraquinone derivatives are usually formed.

It seemed to us that the following method might be a very satisfactory one, not only for the synthesis of phenolphthalein and isophenolphthalein but also for a variety of diarylphthalides, since only one phthalide could be produced and the formation of an anthraquinone would be impossible; moreover, due to the procedure employed, the positions of any substituents in the phthalide molecule would be known with certainty.

Benzophenone should yield the MgBr derivative of 2-methyltriphenyl-

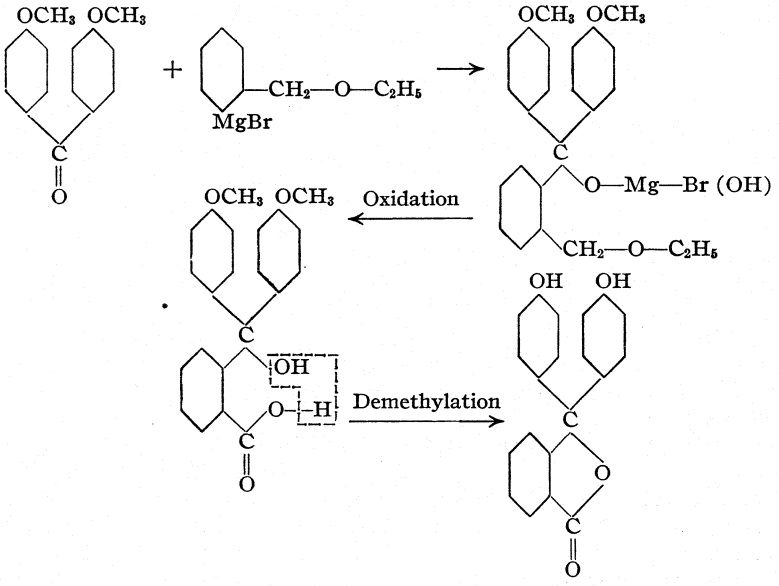
[1] This paper represents the first part of a dissertation submitted to the Graduate School by O. J. Weinkauff in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan. We wish to take this opportunity to acknowledge our indebtedness to The Upjohn Company, who have made this investigation possible by the grant of a fellowship.

[2] Pasternack, U. S. Patent, 1,681,361 (1928).

[3] Hatcher, see Orndorff and Barrett, THIS JOURNAL, **46**, 2487 (1924).

carbinol when treated with 2-methylphenylmagnesium bromide. Upon hydrolysis of this compound to the carbinol and oxidation of the methyl group to carboxyl, with spontaneous elimination of water from the molecule, diphenylphthalide should be formed. Although we were able by this method to obtain diphenylphthalide from benzophenone, and fluoran from 2,2′-dimethoxybenzophenone, the yields of the phthalides were low due to the difficulty encountered in the oxidation of the methyl group. However, by a slight modification of the above procedure, namely, the use of the Grignard reagent prepared from 2-ethoxymethylphenyl bromide instead of that from 2-methylphenyl bromide, it was found possible to prepare diphenylphthalide, phenolphthalein, isophenolphthalein and fluoran in fairly good yields.

The following series of reactions illustrates the process for the preparation of phenolphthalein[4]




We attempted to prepare isophenolphthalein by the method of Orndorff and Barrett.[5] According to these investigators this product was obtained

[4] We have not been able by the use of the method described above to prepare certain mono- and dihydroxydiarylphthalides although the syntheses of the corresponding tertiary carbinols have been described in the experimental part of the paper; in some cases the compounds seemed to decompose during the oxidation of the side chain, in others during demethylation. The applicability of the procedure for the preparation of a number of other substituted diarylphthalides is under investigation and it has been found, so far, that 3′,3″-dibromophenolphthalein can be obtained from 3,3′-dibromo-4,4′-dimethoxybenzophenone.

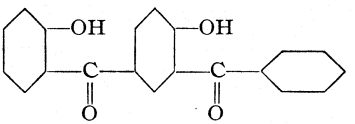
[5] Orndorff and Barrett, THIS JOURNAL, 46, 2488 (1924).

by them in 87% yield from the condensation of 2-(2′-hydroxybenzoyl)-benzoic acid with phenol in the presence of stannic chloride at 100–110°. Although the procedure was repeated a number of times and various condensation agents were used, we were unable to isolate any of the desired product. Instead there was obtained *phenolphthalein* in 40% yield, a small quantity of fluoran and a tar. It is possible, of course, that the latter may have contained some isophenolphthalein. Orndorff and Barrett make no mention of phenolphthalein as a reaction product. The formation of the latter was entirely unexpected and it was thought that the 2-(2′-hydroxybenzoyl)-benzoic acid used might possibly have been contaminated with 2-(4′-hydroxybenzoyl)-benzoic acid, although the amount of the latter, even if present, could hardly have been great enough to produce phenolphthalein in the yield stated above. 2-(2′-Hydroxybenzoyl)-benzoic acid was subjected to a very thorough process of purification but when the highly purified acid was used phenolphthalein was obtained again in a yield approximately that given above.

## Experimental Part

**2-Hydroxybenzophenone.**—Salicylic acid was converted into the methyl ether of methyl salicylate,[6] the latter was hydrolyzed to the methyl ether of salicylic acid and the acid was then treated with thionyl chloride.[7] The crude acid chloride, obtained from 80 g. of the methyl ether, was dissolved in 400 cc. of thiophene-free benzene and 80 g. of aluminum chloride was added, in portions, during the course of an hour. After several hours the mixture was decomposed with ice and hydrochloric acid, the benzene layer separated, dried and the excess benzene removed. After the oil had remained at ordinary temperature for several months, 10 g. of crystalline material had formed. The latter was separated and the oil, which consisted to a large extent of 2-hydroxybenzophenone, was distilled with superheated steam; the oily distillate, which solidified when cooled, was recrystallized from alcohol. Sixty grams of 2-hydroxybenzophenone was obtained, m. p. 40–41°.

The crystalline material mentioned above melted at 131–132° after recrystallization from alcohol. It was found to be soluble in aqueous sodium hydroxide, benzene and hot acetic acid and was slightly soluble in ether. It dissolved in concd. sulfuric acid with the formation of a yellow solution. One gram of the material was fused with potassium hydroxide. There was obtained 0.43 g. of a compound which after recrystallization from water melted at 147–148°. This substance proved to be 2,4′-dihydroxybenzophenone, mixed m. p. 147–149°. An analysis and a molecular weight determination of the compound which melted at 131–132° yielded data which correspond to those calculated for $C_{20}H_{14}O_4$. The material is probably 2-hydroxy-5-(2′-hydroxy-benzoyl)-benzophenone,[8] (A) formed by the further re-



A

[6] Graebe, *Ann.*, **340**, 210 (1905); Sachs and Herold, *Ber.*, **40**, 2718 (1907).

[7] E. Fischer and Slimmer, *ibid.*, **36**, 2585 (1903).

[8] As a by-product from the synthesis described above Graebe and Ullmann [*ibid.*, **29**, 824 (1896)] obtained a substance which melted at 127° and stated that the analytical results checked most closely to those calculated for a dihydroxybenzophenone.

action of the acid chloride on the primary reaction product, 2-methoxybenzophenone, and subsequent demethylation by the aluminum chloride.

*Anal.* Calcd. for $C_{20}H_{14}O_4$: mol. wt., 318; C, 75.46; H, 4.40. Found: mol. wt. (diphenyl),[9] 320: C, 75.35; H, 4.50.

The 4-nitrobenzyl ether of the hydroxy ketone was prepared in the following manner: one hundredth mole of 2-hydroxybenzophenone and 0.01 mole of 4-nitrobenzyl bromide were dissolved in 15 cc. of acetone. One hundredth mole of crystalline sodium hydroxide and 5 cc. of water were added and the mixture heated on a steam-bath for one hour. The ether, which separated in crystalline form, melted at 124–125° after recrystallization from acetone.

**4-Hydroxybenzophenone.**—Twelve and two-tenths grams of benzoic acid, 9.4 g. of phenol and 26 g. of stannic chloride were placed in a flask connected with a reflux condenser and the mixture was heated in a bath at 120° for eighteen hours. After the addition of about 20 cc. of hydrochloric acid, the mixture was filtered. The solid material was treated with 10% aqueous sodium carbonate, which dissolved the benzoic acid and the hydroxybenzophenone. Carbon dioxide was passed into the alkaline solution, whereupon the hydroxy ketone precipitated. The yield of the latter was 4 g.; 6.5 g. of benzoic acid was recovered. After recrystallization of the hydroxy ketone from water, it melted at 135–136°.[10] When an equivalent amount of phenyl benzoate was used in place of benzoic acid, there was obtained 1.5 g. of the ketone and 5 g. of unchanged ester.

**2,4′-Dihydroxybenzophenone.**—(a) A mixture prepared from 10.6 g. of salol and 13 g. of stannic chloride was heated under reflux for eighteen hours at 115–120° in an oil-bath. The reaction product was treated with hot hydrochloric acid in order to remove unchanged stannic chloride, cooled and filtered. After recrystallization from water the hydroxy ketone melted at 147–149°,[11] yield 5.8 g.

(b) Thirteen grams of salicylic acid, 9.4 g. of phenol and 26 g. of stannic chloride were heated under reflux for eighteen hours at 120°. There was obtained 5.5 g. of 2,4′-dihydroxybenzophenone and 4.5 g. of salicylic acid; in one instance we were able to isolate a small quantity of 4,4′-dihydroxybenzophenone.[12]

The dimethyl ether of 2,4′-dihydroxybenzophenone melted at 99–100°.[13]

**3,4′-Dimethoxybenzophenone.**—One hundred thirty-five grams of 3-methoxybenzoic acid[14] was treated with 330 g. of thionyl chloride. After twenty-four hours the excess thionyl chloride was removed under diminished pressure and the acid chloride distilled, b. p. 122–123° under 16 mm. pressure. The yield was 118 g. Eighty-five grams of the acid chloride was dissolved in 50 cc. of tetrachloroethane and added, drop by drop, to a mixture of 65 g. of anisole, 85 g. of aluminum chloride and 100 cc. of tetrachloroethane. After forty-eight hours the reaction mixture was decomposed with ice and hydrochloric acid and the tetrachloroethane and excess anisole removed by steam distillation. The oily product was shaken with 10% sodium hydroxide solution, whereupon it became solid. After recrystallization from alcohol it melted at 58–59°. The yield was practically quantitative.[15]

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[9] Purified according to the method of Chipman and Peltier, *Ind. Eng. Chem.*, **21**, 1106 (1929).

[10] Döbner, *Ann.*, **210**, 251 (1881).

[11] Several investigators have reported that this substance melts at 142–144° although Baeyer [*Ann.*, **354**, 178 (1907)] stated that the compound melts at 150–151°.

[12] Michael, *Am. Chem. J.*, **5**, 83 (1883); Baeyer, *Ann.*, **354**, 177 (1907).

[13] Stoermer, *Ber.*, **41**, 323 (1908).

[14] Graebe, *Ann.*, **340**, 211 (1905).

[15] Lea and Robinson [*J. Chem. Soc.*, 2355 (1926)] obtained only a 40% yield of

**2-(2'-Hydroxybenzoyl)- and 2-(4'-Hydroxybenzoyl)-benzoic Acids.**—These compounds were prepared according to the method of Ullmann and Schmidt[16] but we obtained much higher yields and different relative amounts of the two acids. The average result from a number of experiments was as follows. From the interaction of 40 g. of pure phthalic anhydride, 40 g. of phenol and 120 g. of aluminum chloride there were isolated 36 g. of the 4'-hydroxy acid which melted at 205–207°, 16 g. of the 2'-hydroxy acid, m. p. 171–173°, and 4 g. of crude phenolphthalein.

**Attempts to Prepare Isophenolphthalein from 2-(2'-Hydroxybenzoyl)-benzoic Acid.**—In order to obtain 2-(2'-hydroxybenzoyl)-benzoic acid entirely free from the 4'-hydroxy isomer, the former acid was recrystallized four times from methyl alcohol, converted into the ethyl ester and the latter hydrolyzed; the acid obtained melted at 171–173°.

The pure 2-(2'-hydroxybenzoyl)-benzoic acid, prepared as described above, was condensed with phenol according to the method of Orndorff and Barrett.[17] There was obtained phenolphthalein in 40% yield, a small amount of fluoran and a tar. When the phenolphthalein was fused with potassium hydroxide, 4,4'-dihydroxybenzophenone was isolated in 85% yield.

**Methylation of Phenolphthalein and Demethylation of Phenolphthalein Dimethyl Ether.**—Fifteen grams of phenolphthalein was dissolved in 200 cc. of 10% sodium hydroxide solution and 35 cc. of dimethyl sulfate was added, in portions, while the mixture was shaken vigorously. Ten grams of sodium hydroxide was added and the solution heated for one-half hour under reflux. An oil separated which became solid when cooled. After recrystallization from alcohol the phenolphthalein dimethyl ether[18] melted at 101–102°; yield 14.7 g. or 90% of the calculated amount.

Demethylation was effected in the following manner. Five grams of the ether, 40 cc. of acetic acid and 25 cc. of 48% hydrobromic acid were refluxed for five hours in a flask fitted to a reflux condenser by means of a ground-glass connection. Most of the hydrobromic and acetic acid was removed by distillation under diminished pressure. The yield of crude phenolphthalein was 3.8 g.; after recrystallization from dilute alcohol it melted at 252–253°.

The ether can also be demethylated if a mixture, prepared from 1 g. of the material, 30 cc. of dry thiophene-free benzene and 2.2 g. of aluminum chloride, is refluxed for two hours.

**Preparation of Tertiary Carbinols.**—The tertiary carbinols were prepared by the action of 2-methylphenylmagnesium bromide and 2-ethoxymethylphenylmagnesium bromide, respectively, on various ketones. 2-Ethoxymethylbromobenzene, necessary for the preparation of the Grignard reagent, was obtained in the following manner. Two hundred and fifty grams of pure 2-bromotoluene was brominated in a flask connected to a reflux condenser by means of a ground-glass connection.[19] The 2-bromobenzyl bromide, which boiled at 130–136° under 16 mm. pressure, was used for the subsequent procedure. One hundred and twenty-six grams of 2-bromobenzyl bromide was added to a cold solution of sodium ethylate prepared from 250 cc. of absolute alcohol and 14 g. of

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the ketone, possibly due to the fact that carbon disulfide was used as a solvent; they reported the melting point to be 55°.

[16] Ullmann and Schmidt, *Ber.*, **52**, 2106 (1919). See also Thiel and Müller, *ibid.*, **55**, 1314 (1922).

[17] Orndorff and Barrett, THIS JOURNAL, **46**, 2488 (1924).

[18] This compound has been obtained by Grande, *Gazz. chim. ital.*, **26**, I, 223 (1896); Underwood and Barker, THIS JOURNAL, **52**, 4084 (1930), and by Herzig and Meyer, *Monatsh.*, **17**, 430 (1896).

[19] Jackson, *Am. Chem. J.*, **1**, 101 (1879–1880).

## TABLE I

### TERTIARY CARBINOLS

The letter in parentheses before the ketone indicates the Grignard reagent used: A, 2-methylphenylmagnesium bromide; B, 2-ethoxymethylphenylmagnesium bromide.

| | Carbinol obtained,[a] -triphenylcarbinol | Grignard reagent and substituted benzophenone | Color with $H_2SO_4$ | M. p., °C. | Formula | Calcd., % C | Calcd., % H | Found, % C | Found, % H |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2-Methyl- | (A) Benzophenone | Yellow | 100–101[b] | $C_{20}H_{18}O$ | ... | .. | ... | .. |
| 2 | 2-Methyl-2′,4″-dimethoxy- | (A) 2,4′-Dimethoxy- | Orange | 152–154 | $C_{22}H_{22}O_3$ | 79.04 | 6.59 | 78.89 | 6.67 |
| 3 | 2-Methyl-4′,4″-dimethoxy- | (A) 4,4′-Dimethoxy-[c] | Orange | 109–110 | $C_{22}H_{22}O_3$ | 79.04 | 6.59 | 78.70 | 6.75 |
| 4 | 2-Ethoxymethyl- | (B) Benzophenone | Yellow | 81– 82 | $C_{22}H_{22}O_2$ | 83.02 | 6.92 | 83.10 | 6.88 |
| 5 | 2-Ethoxymethyl-2′-methoxy- | (B) 2-Methoxy- | Green turns to red | 108–109 | $C_{23}H_{24}O_3$ | 79.27 | 6.90 | 79.26 | 6.90 |
| 6 | 2-Ethoxymethyl-3′-methoxy- | (B) 3-Methoxy-[d] | ..... | Oily | $C_{23}H_{24}O_3$ | 79.27 | 6.90 | .. | .. |
| 7 | 2-Ethoxymethyl-4′-methoxy- | (B) 4-Methoxy- | Orange | 100–101 | $C_{23}H_{24}O_3$ | 79.27 | 6.90 | 79.10 | 6.98 |
| 8 | 2-Ethoxymethyl-2′,2″-dimethoxy- | (B) 2,2′-Dimethoxy-[e] | Blue turns to purple | 103–104 | $C_{24}H_{26}O_4$ | 76.19 | 6.88 | 76.06 | 6.94 |
| 9 | 2-Ethoxymethyl-2′,4″-dimethoxy- | (B) 2,4′-Dimethoxy- | Red | 107–108 | $C_{24}H_{26}O_4$ | 76.19 | 6.88 | 75.97 | 6.93 |
| 10 | 2-Ethoxymethyl-4′,4″-dimethoxy- | (B) 4,4′-Dimethoxy- | Orange-red | 74– 76 | $C_{24}H_{26}O_4$ | 76.19 | 6.88 | 75.80 | 6.67 |
| 11 | 2-Ethoxymethyl-3′,4″-dimethoxy- | (B) 3,4′-Dimethoxy- | Orange-red | 83– 84 | $C_{24}H_{26}O_4$ | 76.19 | 6.88 | 75.82 | 7.10 |
| 12 | 9-(2′-Methylphenyl)-xanthydrol[f] | (A) Xanthone | Yellow | 165–166 | $C_{20}H_{16}O_2$ | 83.33 | 5.56 | 83.40 | 5.65 |
| 13 | 9-(2′-Ethoxymethylphenyl)-xanthydrol | (B) Xanthone | Yellow | 153–154 | $C_{22}H_{20}O_3$ | 79.52 | 6.02 | 79.44 | 6.06 |

[a] Carbinols 1, 2, 7, 9 and 12 were recrystallized from a mixture of benzene and petroleum ether (30–60°); 4 and 5 from a mixture of high (90–120°) and low boiling petroleum ether (30–60°); 8 and 11 from methyl alcohol, 13 from benzene and 3 and 10 from alcohol. [b] Bistrzycki and Gyr, *Ber.*, **37**, 1248 (1904), recorded the melting point as 98°. [c] Baeyer and Burkhardt, *Ann.*, **202**, 126 (1880); Zincke and Birschell, *ibid.*, **362**, 226 (1908); Blicke and Smith, THIS JOURNAL, **51**, 1872 (1929). [d] Ullmann and Goldberg, *Ber.*, **35**, 2814 (1902). [e] Richter, *J. prakt. Chem.* [2] **28**, 285 (1883); Graebe and Feer, *Ber.*, **19**, 2610 (1886). [f] Decker and Fellenberg, *Ann.*, **356**, 309 (1907), obtained a compound from xanthone and 2-tolylmagnesium bromide which they claimed was 9-(2′-methylphenyl)-xanthydrol. Their material consisted of "pseudo crystals" which melted at 150.5° The product obtained by us consisted of well-defined colorless glistening crystals.

sodium. The mixture was heated for two hours on a steam-bath. The sodium bromide was removed and the greater part of the alcohol distilled. The residue was poured into water and the oil which separated was treated successively with a concd. sodium bisulfite solution,[20] water and dilute aqueous sodium carbonate. The oil was dried and distilled; b. p. 108–109° under 13 mm. pressure.

To the Grignard reagent prepared from 0.1 mole of 2-methylbromobenzene or 2-ethoxymethylbromobenzene, 0.1 mole of magnesium, a few crystals of iodine and a mixture composed of 25 cc. of ether and 25 cc. of dry benzene, there was added 0.07 mole of the ketone, dissolved or suspended in 50 cc. of dry benzene. During the preparation of the Grignard reagent a stream of dry nitrogen was passed over the top of the condenser. The mixture was heated on a steam-bath for three hours and then decomposed with ice and ammonium chloride. The crude carbinols were subjected to steam distillation for several hours, then dried and purified by recrystallization.

The carbinols which were prepared are listed below. The method of preparation is indicated in Table I.

**Oxidation of Tertiary Carbinols to Dimethyl Ethers of Diarylphthalides.**—In many instances the oxidation of the methyl group to carboxyl in the carbinols which contained a tolyl nucleus did not take place readily and we were able, only in a few cases, to prepare the desired phthalide from such carbinols. The oxidation of 9-(2′-methylphenyl)-xanthydrol to fluoran was accomplished as follows. A solution prepared from 0.50 g. of the carbinol, 20 cc. of concd. sulfuric acid and 50 cc. of water was heated to the boiling point. Five-tenths of a gram of sodium dichromate, dissolved in 5 cc. of water, was added to the hot solution. The latter was stirred thoroughly and boiled for ten minutes. The mixture was cooled, water was added and the solid material removed by filtration.

TABLE II

DIMETHYL ETHERS OF DIARYLPHTHALIDES

| Carbinol | Oxidation product[a] | M. p., °C. |
|---|---|---|
| 1, 4 | Diphenylphthalide | 114–115[b] |
| 5 | 2′-Methoxydiphenylphthalide | 127–128 |
| 6 | 3′-Methoxydiphenylphthalide | Gum |
| 7 | 4′-Methoxydiphenylphthalide | Gum[c] |
| 8 | 2′,2″-Dimethoxydiphenylphthalide | 151–152[d] |
| 9 | 2′,4″-Dimethoxydiphenylphthalide | 127–128[e] |
| 10 | 4′,4″-Dimethoxydiphenylphthalide | 101–102[f] |
| 11 | 3′,4″-Dimethoxydiphenylphthalide | 200–201[g] |
| 12, 13 | Fluoran | 182–183[h] |

[a] All of the ethers were recrystallized from alcohol except the compound obtained from carbinol 11; this substance was recrystallized from toluene. [b] V. Pechmann [*Ber.*, **14**, 1866 (1881)] recorded the melting point as 115°. [c] H. Meyer and O. Fischer [*ibid.*, **44**, 1953 (1911)] stated that this compound melts at 86°; they experienced difficulty in obtaining it in crystalline form. [d] Ferrario [*Gazz. chim. ital.*, **41**, I, 1 (1911)] stated that this substance melts at 145–146°. [e] Orndorff and Barrett [THIS JOURNAL, **46**, 2490 (1924)] found the melting point to be 122°. [f] Grande [*Gazz. chim. ital.*, **26**, I, 224 (1896)] recorded the melting point as 101–102°. [g] This compound is insoluble in ether, soluble in hot toluene and dissolves in concd. sulfuric acid with the formation of a violet solution. *Anal.* Calcd. for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 75.94; H, 5.17. [h] Ferrario [*Gazz. chim. ital.*, **41**, I, 10 (1911)] recorded the melting point as 182°.

[20] To remove any aldehyde present; Errera, *Gazz. chim. ital.*, **17**, 204, 208 (1887).

TABLE III

HYDROXYDIARYLPHTHALIDES

Prepared by demethylation of the oxidation products (dimethyl ethers of diarylphthalides) listed in Table II.[a]

| | | M. p., °C. |
|---|---|---|
| 7[b] | 4′-Hydroxydiphenylphthalide | Amorphous |
| 8 | Fluoran | 182–183[c] |
| 9 | Isophenolphthalein | 198–199[d] |
| 10 | Phenolphthalein | 254–255[e] |
| 11 | 3′,4″-Dihydroxydiphenylphthalide | Amorphous[f] |

[a] Demethylation was effected with hydrobromic acid in the manner described in the case of phenolphthalein dimethyl ether. [b] These numbers refer to the tertiary carbinols from which the hydroxydiarylphthalides were obtained. [c] Ferrario [*Gazz. chim. ital.*, **41**, I, 10 (1911)] recorded the melting point as 182°. [d] Orndorff and Barrett [THIS JOURNAL, **46**, 2485 (1924)] stated that the compound melted at 200°. [e] Bebie [*J. Am. Pharm. Assoc.*, **19**, 372 (1930)] reported the melting point as 262.8° (corr.). [f] This material dissolved in alkali to form a red solution.

After recrystallization from alcohol, there was obtained 0.22 g. of crystalline fluoran; mixed m. p. 181–182°.

The oxidation of the ethoxymethyl group to carboxyl is illustrated by the conversion of 2-ethoxymethyl-4′,4″-dimethoxytriphenylcarbinol into the dimethyl ether of phenolphthalein. Five grams of the carbinol, 10.5 g. of finely powdered sodium dichromate and 100 cc. of acetic acid were refluxed for two hours. The mixture was treated with 400 cc. of hot water and after some time the gummy precipitate was removed and recrystallized from alcohol. Three and one-tenth grams of material was obtained which melted at 97–99°. After further recrystallization the phenolphthalein dimethyl ether melted at 101–102°; yield 70% of the calculated amount.

The yields obtained in the oxidation of other carbinols varied from 40–60%. In the case of some of the dimethoxydiarylphthalides considerable difficulty was experienced in their purification.

The oxidation products obtained from other carbinols are recorded in Table II.

## Summary

It has been found that the interaction of 2-ethoxymethylphenylmagnesium bromide with the methyl ethers of various hydroxybenzophenones yields tertiary carbinols in which the ethoxymethyl group can be oxidized to carboxyl with the spontaneous formation of methyl ethers of diarylphthalides Upon demethylation hydroxydiarylphthalides are obtained.

This method is of advantage in that phthalides so formed cannot be contaminated with isomeric phthalides or anthraquinone compounds and, due to the method of synthesis, the positions of any substituents in the phthalide molecule are known with certainty.

This procedure has been found satisfactory for the preparation of diphenylphthalide, phenolphthalein, isophenolphthalein and fluoran.

Preliminary tests indicate that isophenolphthalein has no laxative effect on humans.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

# THE PREPARATION OF 2-(4″-HYDROXYBENZOYL)-4′-HYDROXYBENZOPHENONE[1]

BY F. F. BLICKE AND O. J. WEINKAUFF

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The preparation of phenolphthalein dimethyl ether (4′,4″-dimethoxydiphenylphthalide) was attempted from phthalic anhydride and 4-methoxyphenylmagnesium iodide. Bauer[2] prepared diphenylphthalide in good yield from phthalic anhydride and phenylmagnesium bromide[3] and by the use of the anhydride mentioned above and 2-methoxyphenylmagnesium iodide Ferrario[4] obtained 2′,2″-dimethoxydiphenylphthalide which, upon demethylation, yielded fluorane.

From phthalic anhydride and 4-methoxyphenylmagnesium iodide, and also from the methyl ester of 2-(4′-methoxybenzoyl)-benzoic acid and the Grignard reagent, we obtained a product which melted at 157–159°; after demethylation the material melted at 225–226° and dissolved in alkali to form a pale yellow solution. The melting points of phenolphthalein dimethyl ether and of phenolphthalein are 102–103° and 254–255°, respectively. Since the data obtained from an analysis and a molecular weight determination of the product which melted at 157–159° corresponded to that calculated for phenolphthalein dimethyl ether, it was evident that a substance isomeric with the last-named compound had been formed.

A consideration of the possible ways in which phthalic anhydride and 4-methoxyphenylmagnesium iodide may combine shows that after the interaction of equivalent amounts of these substances with the formation of compound I, further reaction of the latter with the Grignard reagent may yield either the dimethyl ether of phenolphthalein (II) or the dimethyl ether of 2-(4-″-hydroxybenzoyl)-4′-hydroxybenzophenone (III), a substance isomeric with phenolphthalein dimethyl ether.

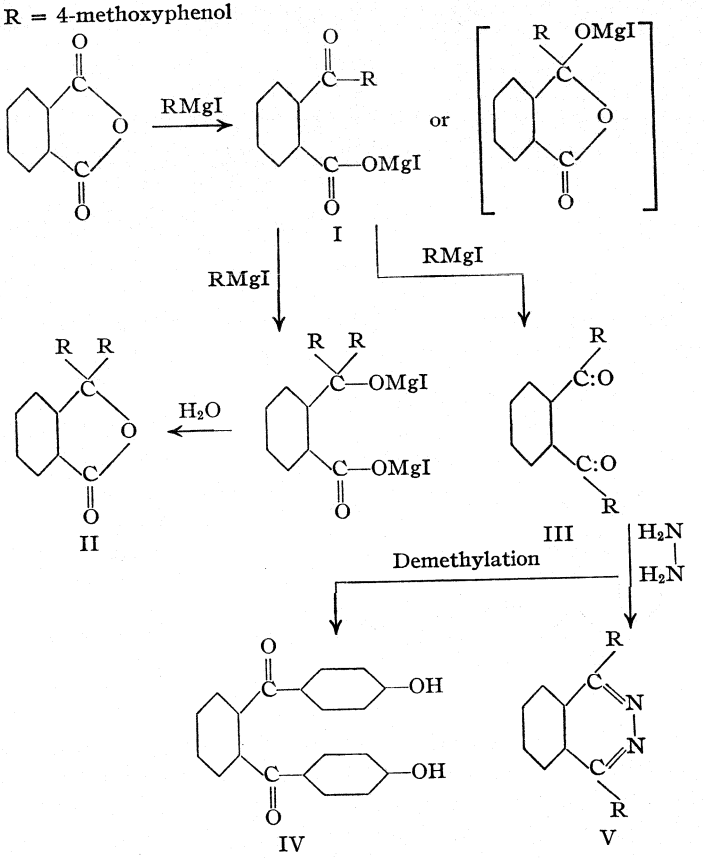
The chemical behavior of the compound (m. p. 157–159°) obtained conformed entirely with that of a substance of structure III. A 1,2-diazine-3,6-di-(*p*-methoxyphenyl)-4,5-benzopyridazine (V), obtained by the action of hydrazine, a dioxime and a diphenylhydrazone were prepared and analyzed. When the compound was fused with potassium hydroxide, 4-methoxybenzoic acid was obtained.

[1] This paper represents the second part of a dissertation submitted to the Graduate School by O. J. Weinkauff in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan. O. J. Weinkauff was awarded The Upjohn Company Fellowship, 1928–1931.

[2] Bauer, *Ber.*, **38**, 240 (1905).

[3] When 4-methoxyphenylmagnesium bromide was used this investigator isolated only gummy material as a reaction product.

[4] Ferrario, *Gazz. chim. ital.*, **41**, I, 1 (1911).

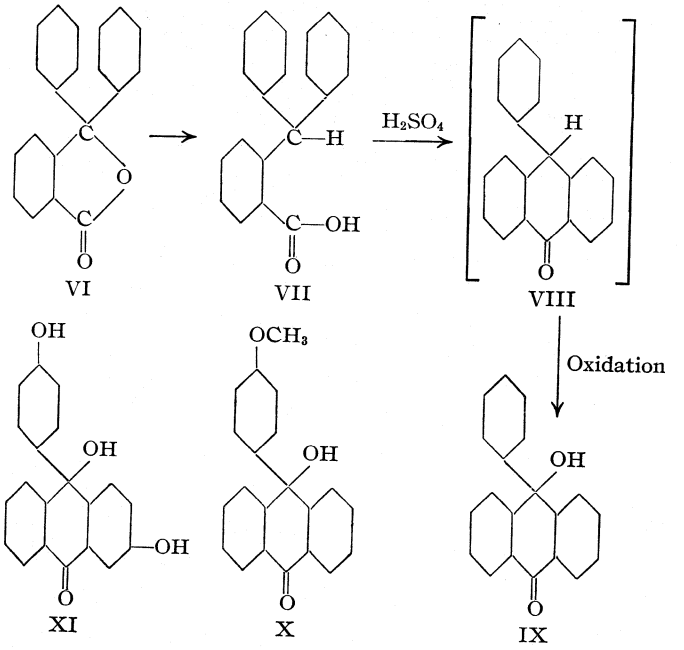



Demethylation of III yielded 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone (IV). This substance, when fused with potassium hydroxide, yielded two molecular equivalents of 4-hydroxybenzoic acid.

A number of years ago Baeyer[5] reduced diphenylphthalide (VI) to triphenylmethane-2-carboxylic acid (diphenylphthalin, VII). The latter, when treated with concentrated sulfuric acid, yielded a substance which, although it was not isolated in pure form nor was its structure suggested,[6] upon oxidation was converted into 9-hydroxy-9-phenylanthrone-10 (IX). Since Haller and Guyot[7] obtained this same compound (IX) from the action of phenylmagnesium bromide on anthraquinone, and these investigators,[8] as well as Liebermann,[9] were able to prepare the corresponding

[5] Baeyer, *Ann.*, **202,** 100 (1880).
[6] Presumably this material was 9-phenylanthrone-10 (VIII).
[7] Haller and Guyot, *Bull. soc. chim.*, [3] **31,** 797 (1904).
[8] Haller and Guyot, *Compt. rend.*, **121,** 102 (1895).
[9] Liebermann, Glawe and Lindenbaum, *Ber.*, **37,** 3337 (1904).

carbinol chloride, there seems to be no doubt regarding the structure of this substance.

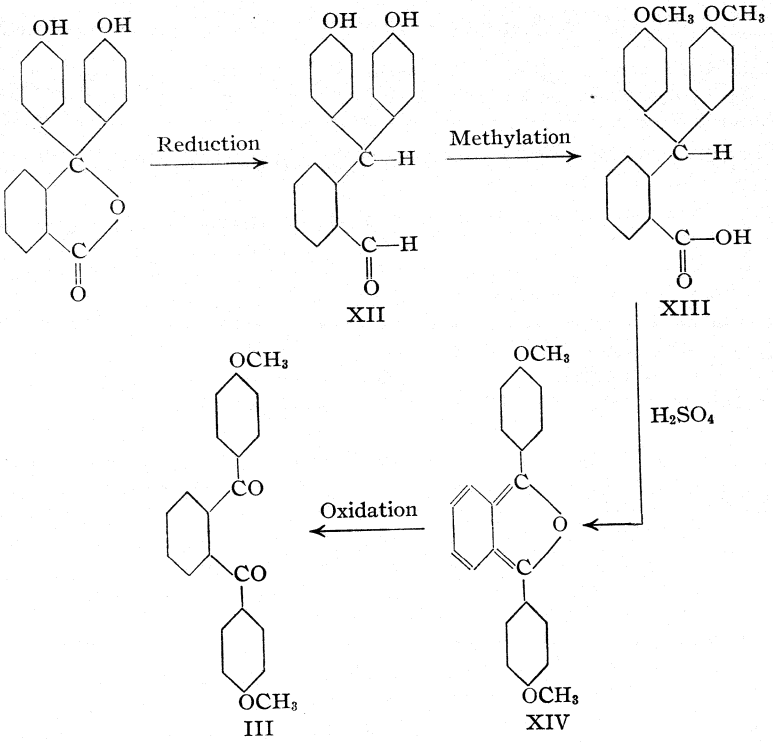



We found that 4-methoxyphenylmagnesium iodide reacts with anthraquinone, analogous to phenylmagnesium bromide, to form 9-(4′-methoxyphenyl)-9-hydroxyanthrone-10 (X).

It might be expected that phenolphthalein-4′,4″-dihydroxydiphenylphthalide—when subjected to the same series of reactions applied in the case of diphenylphthalide, would yield a dihydroxy analog of IX, namely, 3,9-dihydroxy-9-(4′-hydroxyphenyl)-anthrone-10 (XI) and Baeyer[5] considered the compound obtained by him from phenolphthalein to possess structure XI. However, since we found that the product obtained from phenolphthalein by Baeyer's method yielded neither a carbinol chloride nor a fuchsone when treated with hydrogen chloride, the structure previously assigned to the compound (XI) seemed questionable. It was discovered that Baeyer's compound[10] is not an anthranol but is identical with 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone (IV).

When phenolphthalein was reduced to 4′,4″-dihydroxytriphenylmethane-2-carboxylic acid (phenolphthalin, XII), the latter converted into the dimethyl ether (XIII) and then treated as described in the case of diphenylphthalin, the final reaction product was found to be identical with compound III. In this instance we were able to isolate the yellow

[10] Named by him "dihydroxyphenylanthranol" according to the older nomenclature.




intermediate reaction product 2,5-di-(*p*-methoxyphenyl)-3,4-benzofuran (XIV).[11]

## Experimental Part

**2-(4″-Hydroxybenzoyl)-4′-hydroxybenzophenone. (a) From Phthalic Anhydride and 4-Methoxyphenylmagnesium Iodide.**—4-Methoxyphenylmagnesium iodide was prepared from 18.8 g. of 4-iodoanisole, 2 g. of magnesium, 30 cc. of ether and 30 cc. of dry benzene. Four and seven-tenths grams of phthalic anhydride, dissolved in 100 cc. of benzene, was stirred rapidly and the Grignard reagent added to it. The mixture was heated for twelve hours. The precipitate which had formed was removed by filtration and decomposed with ice and ammonium chloride. The product was extracted with benzene and the benzene layer shaken with 10% sodium carbonate solution. After removal of the solvent the solid residue was recrystallized from toluene; m. p. 157–159°. This substance, the dimethyl ether of 2-(4″-hydroxybenzoyl)-4′-hydroxybenzo-

[11] The diphenyl analog of this substance has been prepared from phenylphthalide and phenylmagnesium bromide by Guyot and Catel [*Bull. soc. chim.*, [3] **35,** 1136 (1906)], Guyot and Vallette [*Ann. chim. phys.*, [8] **23,** 372, 388 (1911)] and by Seer and Dischendorfer [*Monatsh.*, **34,** 1495 (1913)]. It has been shown by Guyot and Haller [*Ann. chim. phys.*, [8] **19,** 297 (1910)] that 2-bis-(*p*-dimethylaminophenyl)-phthalide, upon reduction, treatment of the reduced material with acetic acid and finally oxidation of the reaction product, yields 2-(4″-dimethylaminobenzoyl)-4′-dimethylaminobenzophenone; hence the above-mentioned diarylphthalide behaves entirely analogous to phenolphthalein.

phenone, is somewhat soluble in hot alcohol and insoluble in ether. It was demethylated with hydrobromic acid in acetic acid solution.

2-(4″-Hydroxybenzoyl)-4′-hydroxybenzophenone, after recrystallization from acetic acid and then from dilute alcohol, melted at 225–226°. The material is insoluble in ether and benzene.

*Anal.* Calcd. for $C_{20}H_{14}O_4$: mol. wt., 318; C, 75.47; H, 4.40. Found: mol. wt. (alcohol),[12] 322; C, 75.31; H, 4.40.

**(b) From the Methyl Ester of 2-(4′-Methoxybenzoyl)-benzoic Acid and 4-Methoxyphenylmagnesium Iodide.**—The Grignard reagent, prepared from 11.7 g. of 4-iodoanisole, 1,2 g. of magnesium, 25 cc. of ether and 25 cc. of benzene, was added to 10.8 g. of the substituted benzoic acid dissolved in 30 cc. of benzene. The mixture was heated for four hours and then decomposed in the usual manner. The dimethyl ether obtained melted at 157–159°.

**(c) From Phenolphthalein.**—4′,4″-Dihydroxytriphenylmethane-2-carboxylic acid (phenolphthalin) was prepared from U. S. P. phenolphthalein in 96% yield; m. p. 231–232°.[13]

Two hundred and fifty cubic centimeters of concd. sulfuric acid was poured into a beaker and stirred rapidly. Two hundred grams of finely powdered phenolphthalein was added in one portion. After the mixture had been stirred for five minutes the solid material had all dissolved. The solution was then poured into two liters of cold water which was stirred rapidly. The green, granular precipitate was filtered and washed with water. This product dissolved readily in acetone, alcohol, benzene and ether with the formation of solutions which exhibited a strong green fluorescence. The material was dissolved immediately in a mixture of 500 cc. of water and 80 g. of sodium hydroxide. The orange red solution was stirred and a solution prepared from 75 g. of potassium permanganate, 50 g. of sodium hydroxide and 1000 cc. of water was added. After five minutes the manganese salt was removed by filtration. The filtrate was stirred and treated with dilute hydrochloric acid. The precipitated material was filtered, washed with water, dried, recrystallized several times from acetic acid and then from dilute methyl alcohol. Since some of the product remains dissolved in the acetic acid mother liquors, the latter should be concentrated. The yield of the substituted benzophenone was 66 g.; m. p. 224–225°.[14]

**(d) From 4′,4″-Dimethoxytriphenylmethane-2-carboxylic Acid.**—This acid,[15] "prepared from phenolphthalein dimethyl ether," when subjected to the action of sulfuric acid in the manner described above, yielded an intensely yellow material, 2,5-di-(*p*-methoxyphenyl)-3,4-benzofuran (XIV). After recrystallization from a mixture of acetone and alcohol the compound melted at 126–127°. The compound dissolves in ether, benzene and acetic acid to form solutions which possess a green fluorescence.

*Anal.* Calcd. for $C_{22}H_{18}O_3$: mol. wt., 330; C, 80.00; H, 5.45. Found: mol. wt. (benzene),[12] 324; C, 79.78; H, 5.43.

The furan, when oxidized, yielded the dimethyl ether of 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone. Six-tenths of a gram of the furan, dissolved in 10 cc. of hot acetic acid, was mixed with 1 g. of sodium dichromate, 10 cc. of acetic acid and 1 cc. of sulfuric acid. The mixture was heated for ten minutes on a steam-bath. Twenty

[12] Menzies method.

[13] Baeyer, *Ann.*, **202**, 81 (1880).

[14] Baeyer [*ibid.*, **202**, 102 (1880)] recorded the melting point as 212°. We obtained this melting point but after further purification the material melted at the temperature stated above.

[15] Grande, *Gazz. chim. ital.*, **26**, I, 228 (1896).

cubic centimeters of hot water was added and the crystalline precipitate obtained was recrystallized from alcohol. The yield was 0.4 g.; m. p. 157–159°; mixed m. p. 157–159°.

**Alkali Fusions.**—One gram of 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone was fused with 5 g. of potassium hydroxide. The residue was dissolved in a small amount of water, filtered and acidified. Sixty-two hundredths of a gram of 4-hydroxybenzoic acid precipitated; m. p. 209–211°. From the filtrate 0.18 g. more of the acid was obtained upon extraction with ether.

When the dimethyl ether of the substituted benzophenone was fused with potassium hydroxide, 4-methoxybenzoic acid was formed; m. p. 181–183°.

**Derivatives of 2-(4″-Methoxybenzoyl)-4′-methoxybenzophenone. 3,6-Di-(*p*-methoxyphenyl)-4,5-benzopyridazine** (V).—Three and five-tenths grams of the benzophenone was mixed with 20 cc. of acetic acid and to the hot solution there was added, in small portions, a solution prepared from 5 g. of 40% aqueous hydrazine hydrate and 10 cc. of acetic acid. The mixture was refluxed for two hours, an equal volume of water added, the solution cooled, the precipitate filtered and washed with water. Three and three-tenths grams of the diazine was obtained. After recrystallization from acetone the compound melted at 205–206°. It is insoluble in ether but soluble in warm benzene.

*Anal.* Calcd. for $C_{22}H_{18}O_2N_2$: C, 77.18; H, 5.30; N, 8.19. Found: C, 76.89; H, 5.30; N, 8.10.

**Dioxime.**—A solution prepared from 5 g. of hydroxylamine hydrochloride, 100 cc. of methyl alcohol and 10 g. of sodium hydroxide was added to 3.7 g. of the benzophenone dissolved in 100 cc. of methyl alcohol. The mixture was refluxed for two hours, cooled, the precipitate filtered and washed with 50% methyl alcohol. After recrystallization from ethyl alcohol there was obtained 2.3 g. of the oxime, which melted at 177–178° with decomposition. The compound is insoluble in ether and benzene.

*Anal.* Calcd. for $C_{22}H_{20}O_4N_2$: C, 70.20; H, 5.36; N, 7.45. Found: C, 70.61; H, 5.31; N, 7.79.

**Diphenylhydrazone.**—A solution prepared from 2.4 g. of the benzophenone, 4.3 g. of phenylhydrazine and 25 cc. of alcohol was refluxed for twelve hours. The solution was cooled, the precipitate filtered and washed with alcohol. After recrystallization from alcohol, 1 g. of material was obtained which melted with decomposition at 171–173°. The product is soluble in warm benzene but insoluble in ether.

*Anal.* Calcd. for $C_{34}H_{30}O_2N_4$: C, 77.53; H, 5.76; N, 10.64. Found: C, 77.37; H, 5.74; N, 10.83.

## Summary

The dimethyl ether of 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone has been prepared by four methods: (a) from phthalic anhydride and 4-methoxyphenylmagnesium iodide; (b) from the methyl ester of 2-(4′-methoxybenzoyl)-benzoic acid and the Grignard reagent mentioned above; (c) from phenolphthalein; (d) from 4′,4″-dimethoxytriphenylmethane-2-carboxylic acid. The corresponding dihydroxy ketone was obtained by demethylation of the ether.

The compound described in the literature as "dihydroxyphenylanthranol," according to modern nomenclature 3,9-dihydroxy-9-(4′-hydroxyphenyl)-anthrone-10, is in reality 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

# THE PREPARATION OF SEVERAL SUBSTITUTED ANTHRONES[1]

BY F. F. BLICKE AND O. J. WEINKAUFF

RECEIVED AUGUST 22, 1931 PUBLISHED APRIL 6, 1932

In view of the fact that 9-hydroxy-9-phenylanthrone-10 (phenyloxanthranol)[2] and 9,9-diphenylanthrone-10[2b,3] have been isolated as reaction products from the interaction of phthalyl chloride and benzene, it seemed not improbable that corresponding hydroxy compounds, namely, 3,9-dihydroxy-9-(4′-hydroxyphenyl)-anthrone-10 (I), 3-hydroxy-9,9-di-(4′-hydroxyphenyl)-anthrone-10 (II) and possibly, in addition, 3-hydroxy-9,-9,10-tri-(4′-hydroxyphenyl)-9,10-dihydroanthrol-10 (III) might be formed as by-products from the condensation of phthalic anhydride with phenol. Since the cathartic action of yellow phenolphthalein may be due to the presence of these compounds, we wished to prepare them in order that they might be tested for laxative action.

Although Baeyer[4] stated that he had obtained compound I, called by him "dihydroxyphenylanthranol," from phenolphthalein it has been shown[5] that Baeyer's compound is, in reality, 2-(4″-hydroxybenzoyl)-4′-hydroxybenzophenone.

We have not been able, as yet, to obtain the first three substances mentioned above but the methyl ethers of the corresponding 2-hydroxy compounds XI, XV and XVI as well as several other anthraquinone derivatives have been prepared. Upon demethylation of the methoxy derivatives highly colored, gummy or resinous products were obtained, undoubtedly fuchsones, which proved to be very difficult to purify.

It was found that interaction of 4-methoxyphenylmagnesium iodide with anthraquinone and with 2-methoxyanthraquinone yields 9-hydroxy-9-(4′-methoxyphenyl)-anthrone-10 (IV) and 2-methoxy-9-hydroxy-9-(4′-methoxyphenyl)-anthrone-10 (XI), respectively. In the case of the latter compound it was necessary to prove that the Grignard reagent had reacted with carbonyl 9 in the methoxyanthraquinone and not with carbonyl 10; therefore the substance was synthesized according to the scheme shown.

2-Methoxy-9,9-di-(4′-methoxyphenyl)-anthrone-10 (XV) and 2-methoxy-9,9,10-tri-(4′-methoxyphenyl)-9,10-dihydroanthrol-10 (XVI) were obtained by means of the reactions indicated.

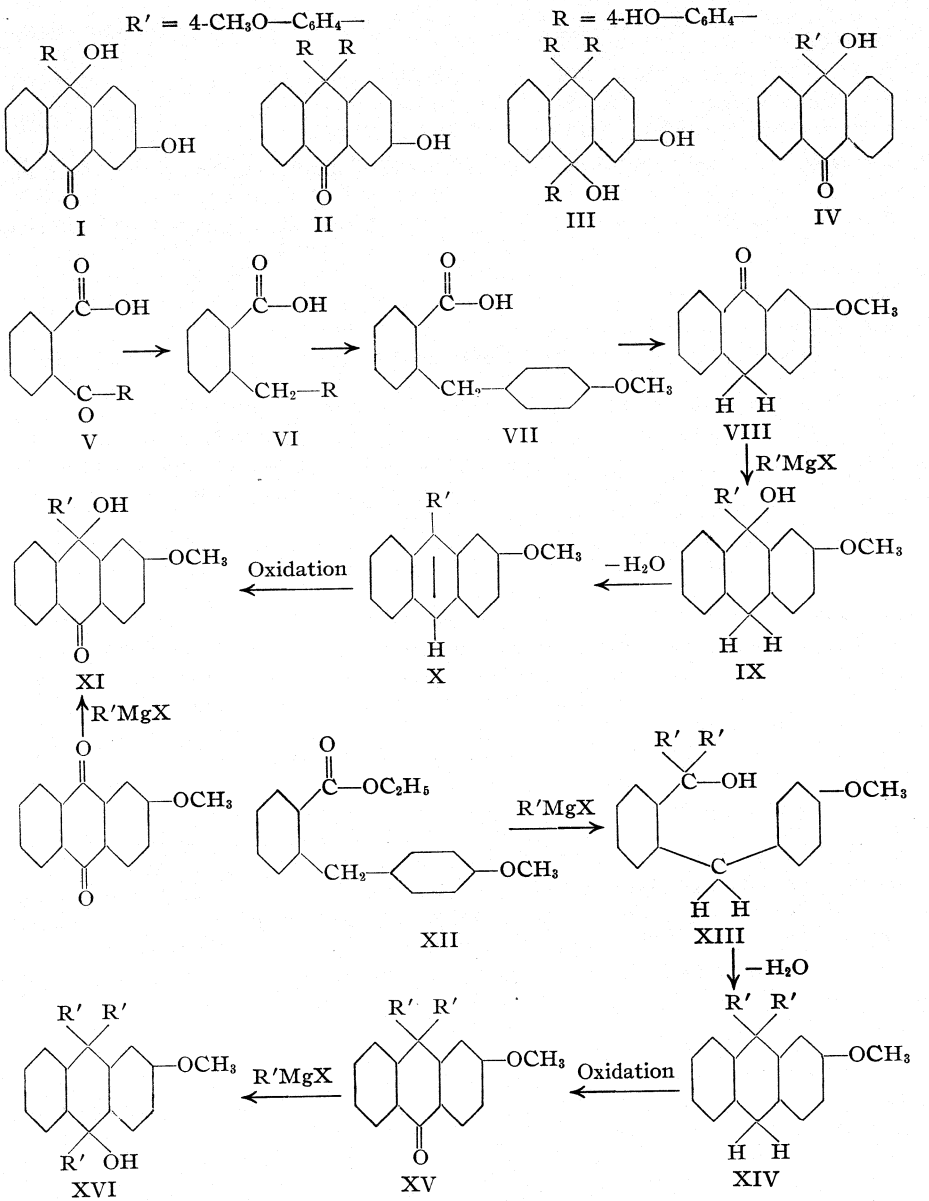
[1] This paper represents the third part of a dissertation submitted to the Graduate School by O. J. Weinkauff in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan. O. J. Weinkauff was awarded The Upjohn Company Fellowship, 1928–1931.

[2] (a) Copisarow, *J. Chem. Soc.*, **111**, 10 (1917); (b) **117**, 209 (1920).

[3] Haller and Guyot, *Bull. soc. chim.*, [3] **17**, 873 (1897).

[4] Baeyer, *Ann.*, **202**, 100 (1880).

[5] Blicke and Weinkauff, THIS JOURNAL, **54**, 1446 (1932).




## Experimental Part

**9-Hydroxy-9-(4′-methoxyphenyl)-anthrone-10 (IV).**—4-Methoxyphenylmagnesium iodide was prepared from 23.4 g. of 4-iodoanisole, 2.4 g. of magnesium and 60 cc. of ether. Forty grams of dry anthraquinone, suspended in 200 cc. of ether, was added to the Grignard reagent while the latter was stirred vigorously. The mixture was heated for two hours on a steam-bath and then decomposed with ice and ammonium chloride.

The ether–benzene solution was separated, filtered, dried and the solvents removed. The solid residue, after recrystallization from alcohol, melted at 206–207°. The material dissolved in concd. sulfuric acid with the formation of a dark green solution.

*Anal.* Calcd. for $C_{21}H_{16}O_3$: mol. wt., 316; C, 79.74; H, 5.06; $OCH_3$, 8.8. Found: mol. wt. (benzene),[6] 314; C, 79.41; H, 5.00; $OCH_3$, 9.8.[7]

**2-(4′-Hydroxybenzyl)-benzoic Acid (VI).**—The following method is a modification of that reported by Bistrzycki and Yssel de Schepper.[8] A solution prepared from 150 g. of 2-(4′-hydroxybenzoyl)-benzoic acid and 2.5 liters of 10% aqueous sodium hydroxide was heated on a steam-bath and stirred rapidly. One hundred and fifty grams of zinc dust was added and the mixture was heated for twenty hours. After filtration the filtrate was acidified and the product recrystallized from alcohol; m. p. 153–154°;[9] yield, 114 g.

**2-Hydroxyanthraquinone from 2-Hydroxyanthrone-9.**—Thirty grams of 2-hydroxyanthrone-9,[8] prepared from 2-(4′-hydroxybenzyl)-benzoic acid, was suspended in 150 cc. of acetic acid and treated with 32 g. of sodium dichromate, dissolved in 15 cc. of hot water, in a flask fitted with a reflux condenser. The mixture soon began to boil. After some time the flask was heated on a steam-bath for about ten minutes, cooled, the crystalline reaction product filtered, washed with acetic acid and then with water. The material weighed 30 g. and melted at 303–304°.[10]

**2-Methoxyanthrone-9 (VIII).**—Since difficulties were encountered in the methylation of 2-hydroxyanthraquinone, the methyl ether of the latter substance was prepared by an indirect method.

The methyl ester of 2-(4′-methoxybenzyl)-benzoic acid (VII) was obtained from 45.6 g. of 2-(4′-hydroxybenzyl)-benzoic acid, 160 cc. of 10% sodium hydroxide solution and 40 cc. of dimethyl sulfate. The ester separated as an oil. In order to hydrolyze the ester, 25 g. of sodium hydroxide was added to the reaction mixture and the latter was refluxed for several hours. The clear, cold solution was acidified. After recrystallization from alcohol the 2-(4′-methoxybenzyl)-benzoic acid melted at 116–117°;[11] yield, 94% of the calculated amount.

Forty-eight and four-tenths grams of finely powdered 2-(4′-methoxybenzyl)-benzoic acid was dissolved in 250 cc. of concd. sulfuric acid which had been cooled to 5°. At the end of three minutes the temperature of the mixture had risen to 25°. The solution was poured immediately into 1.5 liters of ice water. The product was filtered, washed with water and recrystallized from methyl alcohol; m. p. 94–95°; yield of pure product, 30 g.

*Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.32; H, 5.40; $OCH_3$, 13.7. Found: C, 80.11; H, 5.23; $OCH_3$, 13.8.[12]

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[6] Menzies method.

[7] Phenol was used as a solvent [Weishut, *Monatsh.*, **33**, 1165 (1912)]. In this instance, as well as when acetic anhydride was used as a solvent, the apparatus used (Gattermann–Wieland, "Die Praxis des organischen Chemikers," Walter de Gruyter, Berlin and Leipzig, 1928, p. 71) was modified to the extent that a 5-cc. dropping funnel was fused to the carbon dioxide inlet tube. The sample and phenol were placed in the apparatus and the hydriodic acid added through the dropping funnel.

[8] Bistrzycki and Yssel de Schepper, *Ber.*, **31**, 2792 (1898).

[9] Bistrzycki and Yssel de Schepper[8] recorded the melting point as 145–146°.

[10] Liebermann [*Ann.*, **212**, 25 (1882)] recorded the melting point as 302°.

[11] The melting point reported by Nourrisson [*Bull. soc. chim.*, [2] **46**, 206 (1886)] is 110–111°.

[12] Phenol was used as a solvent.

The structure of the methoxyanthrone was proved by its conversion into 2-methoxyanthraquinone by oxidation. Eleven and two-tenths grams of the methoxyanthrone, suspended in 80 cc. of acetic acid, was treated with 11 g. of sodium dichromate, dissolved in 10 cc. of hot water. The mixture soon began to boil. After it had been heated for one hour on a steam-bath it was cooled and the crystalline reaction product recrystallized from acetic acid. Nine and seven-tenths grams of pale yellow 2-methoxyanthraquinone was obtained; m. p. 194–195°.[13]

When 2-hydroxyanthrone was oxidized in the manner described above, 2-hydroxyanthraquinone was formed; m. p. 303–304°.

**2-Methoxy-9-(4′-methoxyphenyl)-anthracene (X).**—4-Methoxyphenylmagnesium iodide was prepared from 23.4 g. of 4-iodoanisole, 2.4 g. of magnesium, 45 cc. of dry benzene and 45 cc. of ether. Nine and four-tenths grams of 2-methoxyanthrone-9, suspended in 50 cc. of benzene, was added to the Grignard reagent and the mixture heated for four hours. After decomposition of the reaction mixture with ice and ammonium chloride, removal of the solvents and steam distillation, 5.2 g. of the anthracene was obtained. After recrystallization from acetic acid and then from benzene–petroleum ether (30–60°) it melted at 175–176°. The compound is very soluble in benzene, slightly soluble in ether and alcohol. The solutions all exhibit a blue fluorescence.

*Anal.* Calcd. for $C_{22}H_{18}O_2$: mol. wt., 314; C, 84.05; H, 5.77; $OCH_3$, 18.5. Found: mol. wt. (benzene), 313; C, 83.72; H, 5.63; $OCH_3$, 19.7.[14]

Because of its instability no attempt was made to isolate the primary product of the reaction, 2-methoxy-9-(4′-methoxyphenyl)-9,10-dihydroanthrol-9 **(IX).**

**2-Methoxy-9-hydroxy-9-(4′-methoxyphenyl)-anthrone-10 (XI).**—Five grams of the above-mentioned anthracene, suspended in 25 cc. of acetic acid, was treated with 3.5 g. of sodium dichromate dissolved in 3 cc. of hot water. The mixture soon began to boil. After the reaction had subsided the mixture was heated on a steam-bath for five minutes, cooled and the crystalline product removed by filtration. The yield was 4.7 g. After recrystallization from acetic acid the anthrone melted at 199–201°. The material is slightly soluble in benzene and insoluble in alcohol and ether.

*Anal.* Calcd. for $C_{22}H_{18}O_4$: mol. wt., 346; C, 76.29; H, 5.24; $OCH_3$, 17.7. Found: mol. wt. (benzene), 362; C, 76.23; H, 5.24; $OCH_3$, 17.9.[15]

The anthrone was also obtained from 2-methoxyanthraquinone and 4-methoxyphenylmagnesium iodide. To the Grignard reagent prepared from 5.8 g. of 4-iodoanisole, 0.6 g. of magnesium and 15 cc. of ether there was added 4.7 g. of 2-methoxyanthraquinone, dissolved in 100 cc. of benzene. The mixture was heated for four hours, decomposed and the reaction product subjected to steam distillation. The gummy residue was dissolved in 10 cc. of hot acetic acid. The solution was allowed to cool, whereupon 1.4 g. of unchanged methoxyanthraquinone separated. This was removed immediately by filtration. After some time 2.3 g. of 2-methoxy-9-hydroxy-9-(4′-methoxyphenyl)-anthrone-10 precipitated from the filtrate. After several recrystallizations from acetic acid the compound melted at 199–200°. The mixed melting point with the substance obtained by oxidation of 2-methoxy-9-(4′-methoxyphenyl)-anthracene was 199–201°.

**2-Methoxy-9,9-di-(4′-methoxyphenyl)-anthrone-10 (XV).**—The ethyl ester of 2-(4′-methoxybenzyl)-benzoic acid (XII) was prepared from the methoxybenzylbenzoic

[13] Graebe and Bernhart [*Ann.*, **349**, 222 (1906)] reported the melting point to be 186.5° while Kaufler [*Ber.*, **37**, 65 (1904)] reported 195–196°.

[14] Acetic anhydride was used as a solvent [Herzig, *Monatsh.*, **9**, 544 (1888)].

[15] Acetic anhydride was used as a solvent.

acid, alcohol and hydrogen chloride. The ester boiled at 214–216° under approximately 10 mm. pressure. Twenty-seven grams of the ester, dissolved in 60 cc. of ether, was added in small portions to the Grignard reagent obtained from 93.6 g. of 4-iodoanisole, 9.6 g. of magnesium and 200 cc. of ether. After the mixture had been heated for four hours, it was decomposed with ice and ammonium chloride. A crystalline by-product, insoluble in the ether layer,[16] was removed by filtration. The ether layer was subjected to steam distillation for some time and the oily product, 2-(4′-methoxybenzyl)-4″,4‴-dimethoxytriphenylcarbinol (XIII), converted into 2-methoxy-9,9-di-(4-methoxyphenyl)-9,10-dihydroanthracene (XIV) in the following manner. The carbinol was dissolved in 150 cc. of acetic acid which had been partially saturated with hydrogen chloride. The deep red solution was heated for two hours on a steam-bath. Most of the solvent was removed from the solution, which had now become brown in color, and the residue was poured into water. The gummy anthracene (XIV), which we could not obtain in solid form, was oxidized to the anthrone. The anthracene, dissolved in 180 cc. of acetic acid, was heated for four hours with 24 g. of sodium dichromate dissolved in 12 cc. of hot water. The greater part of the acetic acid was removed and water was added to the residue. The solid product obtained was recrystallized several times from acetic acid. The yield of the anthrone was 12 g.; m. p. 183–184°.

*Anal.* Calcd. for $C_{29}H_{24}O_4$: C, 79.78; H, 5.54; $OCH_3$, 21.0. Found: C, 79.66; H, 5.38; $OCH_3$, 21.3.[17]

**2-Methoxy-9,9,10-tri-(4′-methoxyphenyl)-9,10-dihydroanthrol-10 (XVI).**—To 4-methoxyphenylmagnesium iodide, prepared from 4.7 g. of 4-iodoanisole, 0.48 g. of magnesium and 15 cc. of ether, there was added 2.18 g. of 2-methoxy-9,9-di-(4′-methoxyphenyl)-anthrone-10 suspended in 50 cc. of benzene. The mixture was heated for four hours, decomposed and the ether–benzene layer subjected to steam distillation. The gummy product, which soon became solid, was recrystallized from alcohol and then from acetic acid; m. p. 193–194°.

*Anal.* Calcd. for $C_{36}H_{32}O_5$: C, 79.37; H, 5.93. Found: C, 78.78; H, 5.86.

## Summary

The preparation of the following compounds has been described: 9-hydroxy-9-(4′-methoxyphenyl)-anthrone-10, 2-hydroxyanthraquinone, 2-methoxyanthrone-9, 2-methoxy-9-(4′-methoxyphenyl)-anthracene, 2-methoxy-9-hydroxy-9-(4′-methoxyphenyl)-anthrone-10, 2-methoxy-9,9-di-(4′-methoxyphenyl)-anthrone-10, 2-methoxy-9,9,10-tri-(4′-methoxyphenyl)-9,10-dihydroanthrol-10.

ANN ARBOR, MICHIGAN

[16] Barnett, Cook and Nixon [*J. Chem. Soc.*, 505 (1927)] obtained a by-product, insoluble in ether, from the interaction of phenylmagnesium bromide and ethyl 2-benzylbenzoate and suggested that the compound might be a pinacol.

[17] Acetic anhydride was used as a solvent.

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

# HALOGEN DERIVATIVES OF DIARYLPHTHALIDES. II[1]

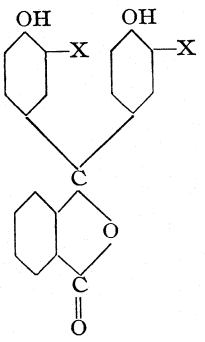
BY F. F. BLICKE, F. D. SMITH AND J. L. POWERS

RECEIVED AUGUST 22, 1931 PUBLISHED APRIL 6, 1932

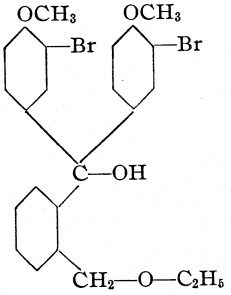
Some time ago[2] we described the products obtained by condensation of 4-fluoro-, 4-chloro-, 4-bromo-, 4-iodo and 3-iodophthalic anhydride with phenol.

We have studied now the interaction of 2-chloro-, 2-bromo, 2-iodo-, 2,6-dichloro- and 2,6-dibromoanisole with phthalyl chloride in the presence of aluminum chloride. The first three compounds reacted at ordinary temperature to form methyl ethers of phthalides of the general structure I in which halogen occupies the X positions; upon demethylation the phthaleins themselves were obtained, substances which dissolve in aqueous sodium hydroxide to form red-violet solutions which fade rapidly.[3]

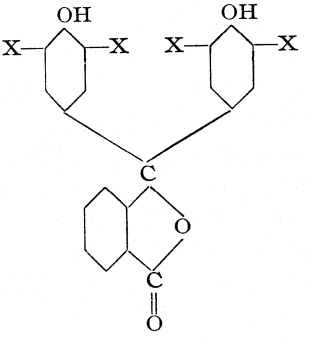
Conclusive proof that the dimethyl ether of the dibromophthalein, and consequently the corresponding dimethyl ethers of the dichloro- and di-iodophthalein, really possessed structure I was obtained by the synthesis of 3′,3″-dibromophenolphthalein dimethyl ether according to a method described previously[4] for the preparation of diarylphthalides. 3,3′-Dibromo-4,4′-dimethoxybenzophenone reacts with 2-ethoxymethylphenylmagnesium bromide to form 2-ethoxymethyl-3′,3″-dibromo-4′,4″-dimethoxytriphenylcarbinol (II).




I




II



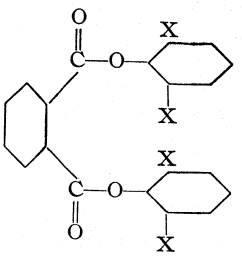

III

[1] This investigation was made possible by a grant from the American Pharmaceutical Association Research Fund and by the establishment of the Michigan State Pharmaceutical Association Research Fund and we wish to acknowledge our appreciation for the aid which has been given us.

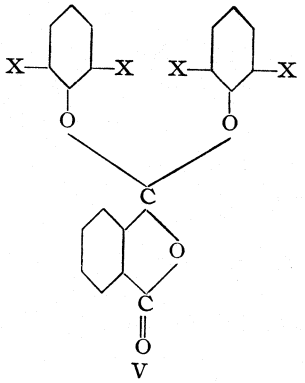
[2] Blicke and Smith, THIS JOURNAL, **51**, 1865 (1929). This publication is to be regarded as the first paper of this series.

[3] Recently Knapp [*Monatsh.*, **56**, 106 (1930)] synthesized a dibromophenolphthalein dimethyl ether from phthalyl chloride, 4-bromoanisole and aluminum chloride. However, the positions of the bromine atoms in the phthalein molecule were not established.

[4] Blicke and Weinkauff, THIS JOURNAL, **54**, 1446 (1932).



IV



V

When this compound was subjected to oxidation the ethoxymethyl group was converted into carboxyl with the spontaneous elimination of water to form the phthalide, a substance which proved to be identical with the compound obtained from phthalyl chloride and 2-bromoanisole[5] and also with the dibromo derivative formed by bromination of phenolphthalein dimethyl ether.[6]

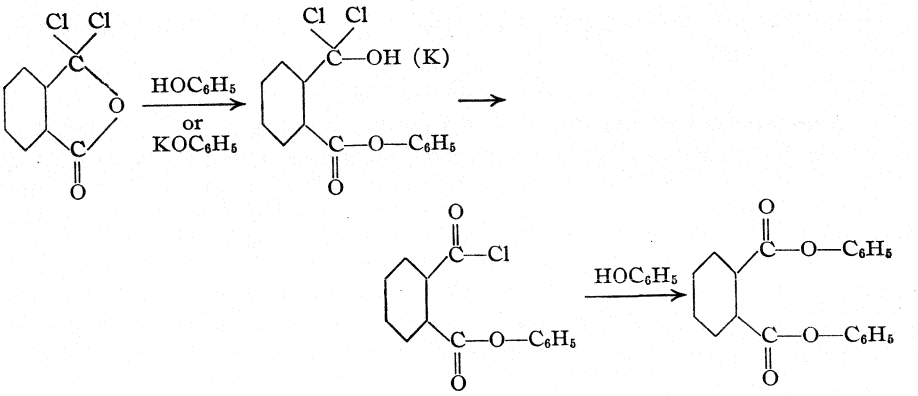
It was thought that from dihaloanisoles and phthalyl chloride methyl ethers of phthaleins of structure III might be produced. However, since it was found necessary in the case of the dihaloanisoles to heat the reaction mixture to the boiling point of the solvent employed, carbon disulfide, the dihaloanisoles were demethylated to a large extent by the aluminum chloride[7] and the phenols formed reacted with the acid chloride to form tetrahalodiphenyl phthalates (IV) the structure of which was proved by their synthesis from phthalyl chloride and potassium 2,6-dihalophenolate. Before we had identified these esters with certainty, it was thought that tetrahalodiphenoxyphthalides of type V might have been produced; hence the synthesis of these compounds was attempted. Since such compounds apparently have not been prepared hitherto in the phthalein series, it was decided to prepare, first, the halogen-free diphenoxyphthalide from unsymmetrical phthalyl chloride and phenol. However, in the case of phenol, as well as potassium phenolate, we obtained diphenyl phthalate instead of diphenoxyphthalide. The following reaction mechanism is suggested to account for the formation of the ester. This mechanism gains support from the fact that phthalic anhydride and phenol react to yield the monophenyl ester of phthalic acid.[8]

[5] Grande [*Gazz. chim. ital.*, **27**, II, 67 (1897)] condensed 2-bromoanisole with phthalyl chloride in the presence of aluminum chloride and obtained a dibromophthalein dimethyl ether which possessed the same melting point as the compound obtained by us.

[6] Grande, *ibid.*, **26**, I, 230 (1896).

[7] Hartmann and Gattermann [*Ber.*, **25**, 3531 (1892)] have shown that anisole is demethylated readily by aluminum chloride.

[8] Bischoff and v. Hedenström, *ibid.*, **35**, 4092 (1902).




Finally, unsymmetrical phthalyl chloride, phenol and aluminum chloride were heated under various conditions but only diphenyl phthalate and a small quantity of phenolphthalein were produced. The latter may possibly have been formed as the result of a Friedel and Crafts reaction, or through the rearrangement of the diphenoxy compound, formed initially as a reaction product, or through the action of aluminum chloride on diphenyl phthalate.[9]

The monohaloanisoles were prepared by catalytic reduction of 2-nitroanisole to 2-anisidine, diazotization of the latter and conversion of the diazonium compound into the desired haloanisole.

2,6-Dichloro- and 2,6-dibromoanisole were obtained in the following manner. 4-Aminobenzoic acid was suspended in hot, dilute sulfuric acid and treated with sodium nitrite. 4-Hydroxybenzoic acid was obtained in 82% yield from a technical grade of the amino acid.[10] By halogenation of the hydroxy acid we obtained 3,5-dichloro-, 3,5-dibromo- and 3,5-diiodo-4-hydroxybenzoic acid.

It was found that carbon dioxide could be eliminated from the dichloro- and dibromohydroxy acids merely by heating them with quinoline in an open flask[11] with a good yield of the corresponding dihalophenol. We were unable to obtain 2,6-di-iodophenol by decarboxylation of 3,5-di-iodo-4-hydroxybenzoic acid, since the phenol underwent decomposition during the process. Our efforts to prepare the phenol methyl ether from 3,5-diiodo-4-methoxybenzoic acid by elimination of carbon dioxide were also unsuccessful.

[9] Csanyi, *Ber.*, **52**, 1792 (1919).

[10] Although this method had been used previously by G. Fischer [*Ann.*, **127**, 145 (1863)], it was stated that considerable resin was formed and that the yield of hydroxy acid was not good.

[11] Several methods which require the use of sealed tubes have been described by Pope and Wood [*J. Chem. Soc.*, **101**, 1827 (1912)] for the elimination of carbon dioxide from 3,5-dibromo-4-hydroxybenzoic acid.

Methylation of the 2,6-dihalophenols with dimethyl sulfate yielded the desired anisoles.

## Experimental Part

**4-Hydroxybenzoic Acid.**—A suspension prepared from 82 g. of 4-aminobenzoic acid (technical grade), 1000 cc. of water and 80 cc. of concd. sulfuric acid was heated to 80° and maintained at this temperature during the following operation. The mixture was stirred mechanically and 41.5 g. of sodium nitrite, dissolved in 300 cc. of water, was introduced slowly below the surface of the liquid. After all of the nitrite had been added, the solution was treated with charcoal, boiled and filtered. About one-half of the hydroxy acid separated from the filtrate when the latter was cooled. The remainder of the acid was obtained by extraction with ether. The crude hydroxy acid was dissolved in hot water and the solution boiled with charcoal until it was obtained, after filtration, in an almost colorless state. The yield was 67 g. or 82% of the calculated amount, m. p. 210–212°.[12]

**2,6-Dichloro- and 2,6-Dibromoanisole.**—We prepared, first, 3,5-dichloro-[13] and 3,5-dibromo-4-hydroxybenzoic acid.[14] The dihalo acids were recrystallized from acetic acid and then thoroughly air-dried. One part of the respective 3,5-dihalo-4-hydroxybenzoic acid was heated in a flask, fitted with an air condenser, with two parts of freshly distilled quinoline until the evolution of carbon dioxide ceased; a bath temperature of 190–200° was required to effect the desired decomposition. The reaction mixture was cooled, treated with an equal volume of concd. hydrochloric acid and then extracted with ether. The ether solution was washed twice with water, separated, dried with fused sodium sulfate and the ether removed. The halophenols became solid when cooled and were recrystallized from petroleum ether (30–60°). The yield of pure product was 80–85%. The phenols were then methylated by the use of dimethyl sulfate.

TABLE I

2,5-DIHALOPHENOLS AND 2,6-DIHALOANISOLES

| | M. p., °C. | B. p., °C. | Formula | Analyses, %[15] Calcd. | Found |
|---|---|---|---|---|---|
| $C_6H_3Cl_2(OH)$ | 68–70 | ..... | ..... | ..... | ... |
| $C_6H_3Cl_2(OCH_3)$ | Liquid | 105–106 (20 mm.) | $C_7H_6OCl_2$ | Cl, 40.11 | 39.70 |
| $C_6H_3Br_2(OH)$ | 55–57 | ..... | ..... | ..... | ... |
| $C_6H_3Br_2(OCH_3)$ | Liquid | 129–130 (20 mm.) | $C_7H_6OCl_2$ | Br, 60.15 | 59.81 |

**Condensation of Phthalyl Chloride with 2-Haloanisoles.**—Two hundredths of a mole of phthalyl chloride was added to 0.05 mole of the respective 2-haloanisole, dissolved in 100 cc. of dry carbon disulfide. During the course of an hour 10 g. of aluminum chloride was added to the mixture. After twenty-four hours the carbon disulfide layer was decanted and the residue decomposed with ice and hydrochloric acid. The product was washed thoroughly with hydrochloric acid, then with sodium hydroxide solution and finally was recrystallized from acetic acid.

**Dihalophenolphthaleins.**—Two grams of the dimethyl ether of the dihalophenolphthalein was dissolved in 50 cc. of boiling acetic acid. Fifty cc. of 48% hydrobromic acid was added to the boiling solution in small portions in order to prevent precipita-

[12] Stohmann, Kleber and Langheim [*J. prakt. Chem.*, [2] **40**, 130 (1889)] recorded the melting point as 213°.

[13] Zincke, *Ann.*, **261**, 250 (1891).

[14] Robertson, *J. Chem. Soc.*, **81**, 1482 (1902).

[15] Thompson-Oakdale method, THIS JOURNAL, **52**, 1195 (1930).

TABLE II

DIMETHYL ETHERS OF 3′,3″-DIHALOPHENOLPHTHALEINS

| | M. p., °C. | Yield,[a] % | Analyses, % Formula $C_{22}H_{16}O_4X_2$ | |
|---|---|---|---|---|
| Dichloro | 136–138 | 90 | Cl, calcd., 17.08 | Found, 17.18 |
| Dibromo | 161–162[b] | 85 | Br, calcd., 31.70 | Found, 31.40 |
| Di-iodo | 177–179 | 66 | I, calcd., 42.47 | Found, 42.40 |

[a] The yield given is that of recrystallized material. [b] Grande [*Gazz. chim. ital.*, [II] **27**, 68 (1897)] found the melting point to be 160–161°.

tion of the phthalein dimethyl ether. The mixture was refluxed for three hours. The hydrobromic and acetic acids were removed and the residue treated with 10% sodium hydroxide solution. The alkaline solution was filtered and then acidified with dilute hydrochloric acid. The phthalein precipitated in an amorphous condition. The iodo compound was obtained in the form of crystals by recrystallization from acetic acid. These dihalophenolphthaleins dissolved in alkali with the formation of red-violet solutions which fade with great rapidity.

TABLE III

3′,3″-DIHALOPHENOLPHTHALEINS

| | M. p., °C. | Analyses, % Formula $C_{20}H_{12}O_4X_2$ | |
|---|---|---|---|
| Dichloro | Amorphous[a] | Cl, calcd., 18.34 | Found, 18.38 |
| Dibromo | Amorphous[b] | Br, calcd., 33.61 | Found, 33.32 |
| Di-iodo | 245–246 | I, calcd., 44.56 | Found, 44.41 |

[a] Consonno and Apostolo [*Gazz. chim. ital.*, [I] **51**, 63 (1921)] stated that they obtained an amorphous phthalein by condensation of phthalic anhydride with 2-chlorophenol but Thiel and Müller [*Ber.*, **55**, 1313 (1922)], who repeated their process, were able to obtain only traces of the compound. Thiel and Diehl [*Sitzber. Ges. Beförder. ges. Naturw. Marburg*, **62**, 536 (1927)] obtained the dichlorophthalein in very satisfactory yield from 2-(3′-chloro-4′hydroxybenzoyl)-benzoic acid and phenol and also from 3′,3″-diaminophenolphthalein. The melting point was recorded as 177°.

[b] This product was obtained by Grande [*Gazz. chim. ital.*, [II] **27**, 69 (1897)] in an amorphous form.

**Condensation of Phthalyl Chloride with 2,6-Dichloro- and 2,6-Dibromoanisole.**—The procedure used was the same as that described above except that the reaction mixture was refluxed for five hours. The compound obtained from 2,6-dichloroanisole, after recrystallization from alcohol, melted at 142–144°. The material obtained from 2,6-dibromoanisole melted at 216–218° after recrystallization from acetic acid.

Tetrachlorodiphenyl and tetrabromodiphenyl phthalate were prepared in the following manner. The potassium derivative was prepared from 2,6-dichlorophenol dissolved in absolute ether. After the addition of one-half of a molecular equivalent of phthalyl chloride the mixture was heated for one hour on a steam-bath. The potassium chloride and ether were removed and the oily residue washed with a small quantity of cold acetic acid. The crystalline material obtained, the 2,2′,6,6′-tetrachlorodiphenyl ester of phthalic acid, was recrystallized from acetic acid; m. p. 142–144°. Mixed with the material obtained from 2,6-dichloroanisole the melting point was unchanged.

*Anal.* Calcd. for $C_{20}H_{10}O_4Cl_4$: mol. wt., 456; Cl, 31.14. Found: mol. wt. (camphor), 434; Cl, 31.42.

When the potassium derivative of 2,6-dibromophenol was used we obtained the 2,2′,6,6′-tetrabromodiphenyl ester of phthalic acid. After recrystallization from acetic

acid the compound melted at 217–218°. The mixed melting point with the substance obtained from 2,6-dibromoanisole was 216–218°.

*Anal.* Calcd. for $C_{20}H_{10}O_4Br_4$: mol. wt., 633; Br, 50.44. Found: mol. wt. (camphor), 632; Br, 49.92.

One and twenty-six hundredths grams of the ester was hydrolyzed. There was obtained 1.00 g. of 2,6-dibromophenol and 0.30 g. of phthalic acid. The calculated amounts of phenol and acid are 1.00 g. and 0.33 g., respectively.

The products we hoped to obtain by condensation of phthalyl chloride with 2,6-dichloro- and 2,6-dibromoanisole were prepared by another method. 3′,3″,5′,5″-Tetrachloro[16] and 3′,3″,5′,5″-tetrabromophenolphthalein[17] were obtained by direct halogenation of phenolphthalein. The melting point of the latter compound was recorded by Baeyer as 220–230° but we found the melting point of tetrabromophenolphthalein to be 295–297°.[18] These halophenolphthaleins were methylated with eight molecular equivalents of dimethyl sulfate in hot alkaline solution. After recrystallization from acetic acid, the dimethyl ether of tetrachlorophenolphthalein melted at 180–182° and the ether of the corresponding tetrabromo compound melted at 201–204°.[19]

*Anal.* Calcd. for $C_{22}H_{14}O_4Cl_4$: Cl, 29.21. Found: Cl, 29.17.

### Preparation of 3′,3″-Dibromophenolphthalein Dimethyl Ether with the Aid of the Grignard Reagent

**2-Ethoxymethyl-3′,3″-dibromo-4′,4″-dimethoxytriphenyl Carbinol.**—2-Ethoxymethylphenylmagnesium bromide was prepared from 4.3 g. of 2-ethoxymethylphenyl bromide, 0.48 g. of magnesium, 10 cc. of ether and 10 cc. of dry benzene. Six grams of 3,3″-dibromo-4,4′-dimethoxybenzophenone,[20] suspended in 25 cc. of benzene, was added and the mixture heated on a steam coil for two hours. After decomposition with ice and ammonium chloride the ether–benzene layer was separated. The crystalline residue, after recrystallization from carbon disulfide, weighed 5.6 g.; m. p. 148°.

**3′,3″-Dibromophenolphthalein Dimethyl Ether.**—To 2.26 g. of the above tertiary carbinol, dissolved in 40 cc. of acetic acid, there was added 3.9 g. of finely powdered potassium dichromate. The mixture was heated with frequent agitation for four hours and then poured into 400 cc. of hot water. After the addition of 10 cc. of hydrochloric acid, the mixture was cooled. The crystalline product, after recrystallization from methyl alcohol, weighed 0.9 g.; m. p. 161–162°. The same melting point was obtained when the product was mixed with the dibromophthalein dimethyl ether produced in the condensation of phthalyl chloride with 2-bromoanisole.

**Attempts to Obtain Diphenoxyphthalide.**—Two grams of unsymmetrical phthalyl chloride,[21] 1.88 g. of phenol and 10 cc. of benzene were heated at 90° for thirty minutes, when the evolution of hydrogen chloride practically ceased. From the reaction mixture there was obtained 2.7 g. of diphenyl phthalate, which melted at 74–75° after recrystallization from alcohol. Complete conversion of the chloride into the ester would have yielded 3.28 g. of the material. No phenolphthalein was formed since the crude reaction product remained colorless when treated with alkali.

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[16] (a) Whiting, THIS JOURNAL, **42**, 2366 (1920); (b) Thiel and Diehl, *Sitzber. Ges. Beförder. ges. Naturw. Marburg*, **62**, 537 (1927).

[17] Baeyer, *Ann.*, **202**, 78 (1880).

[18] Thiel and Diehl[16b] reported the melting point to be 286°.

[19] Meyer, [*Ber.*, **40**, 2432 (1907)] recorded the melting point as 205–206°.

[20] Bösler, *ibid.*, **14**, 329 (1881).

[21] Ott, *Ann.*, **392**, 274 (1912). In order to obtain this compound it is essential that the product obtained after rearrangement of the *sym.* acid chloride with aluminum chloride should be pulverized very finely before it is sifted on ice.

Potassium phenolate was prepared from 9.4 g. of phenol, dissolved in 150 cc. of absolute ether. Seven and five-tenths grams of the acid chloride was added and the mixture heated for thirty minutes. Eleven and three-tenths grams of diphenyl phthalate was isolated; the calculated amount of ester is 12.3 g.

Sixteen grams of aluminum chloride was added, in portions, to a mixture prepared from 10 g. of the acid chloride, 9.4 g. of phenol and 100 cc. of carbon disulfide. The mixture was refluxed for one-half hour, when the evolution of hydrogen chloride stopped. The carbon disulfide, which was found to be free from organic compounds, was decanted and the residue, after decomposition with ice and hydrochloric acid, steam distilled to remove any unchanged phenol. The amorphous reaction product weighed 8.2 g. Two and five-tenths grams of this material was treated with 100 cc. of 2% sodium hydroxide solution. Two grams of an alkali-insoluble product was obtained which proved to be diphenyl phthalate; m. p. 74–75°. Upon acidification of the alkaline solution, 0.2 g. of phenolphthalein precipitated which melted at 254° after recrystallization from acetic acid.

## Summary

2-Chloro-, 2-bromo- and 2-iodoanisole react with phthalyl chloride in the presence of aluminum chloride to yield 3′,3″-dihalophenolphthalein dimethyl ethers. Upon demethylation the phthaleins themselves were obtained.

From 2,6-dichloro- and 2,6-dibromoanisole, phthalyl chloride and aluminum chloride tetrahalodiphenyl phthalates were formed.

A practical method has been found for the preparation of 2,6-dichloro- and 2,6-dibromophenol.

Attempts to obtain diphenoxyphthalide are described.

ANN ARBOR, MICHIGAN

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

# THE BASIS FOR THE PHYSIOLOGICAL ACTIVITY OF -ONIUM COMPOUNDS. IX. DERIVATIVES OF HOMOLOGS OF BETAINE[1]

BY R. R. RENSHAW AND M. E. MCGREAL[2]

RECEIVED AUGUST 22, 1931 PUBLISHED APRIL 6, 1932

The present paper deals with a continuation of the work[3] being done in coöperation with Reid Hunt, in an attempt to get some light on the basis for the action of substances on the nervous system and, along with that, the problem of discovering substances with highly selective actions on such tissues. In the latter endeavor some success has been attained.

[1] This problem is being carried out in coöperation with Dr. Reid Hunt of the Harvard Medical School. The physiological data are the basis of another series of papers published elsewhere by him.

[2] This paper includes a portion of the material of a thesis presented by Martin E. McGreal, June, 1928, for the degree of Doctor of Philosophy at New York University.

[3] Renshaw and co-workers: (a) *Science*, **62**, 384 (1925); (b) THIS JOURNAL, **47**, 1904, (c) 2989 (1925); (d) *ibid.*, **48**, 517, (e) 1726, (f) 2146, (g) 2698 (1926); (h) *ibid.*, **51**, 953 (1929).

Hunt[4] has been able with these various products to obtain better control over the peripheral nervous system than has been possible before.

It has been shown[4g] that the physiologically inert betaine $(CH_3)_3N(CH_2COOH)X$ could be transformed into highly active substances by esterification. The methyl and ethyl esters gave the same type of action on the autonomic nervous system that the salts of choline, $(CH_3)_3N(CH_2CH_2OH)X$ give. Particularly intense was the "muscarine action," which caused a marked fall of blood pressure and, in larger doses, a slowing of the heart from a stimulation of the ending of the vagus nerve in the heart. We have prepared the esters of a number of homologs of betaine with other alkyl amine groups in place of the trimethylamine group in order to determine the effect of this variation on the muscarine and other actions. Hunt and Taveau[4a] had shown that in the choline series the muscarine action was most typical of those compounds having the trimethylamine group. Since that time, it has been shown largely through the work of Hunt and of Dale that many of these compounds also have a stimulating nicotine-like action on the ganglion cells of the autonomic nervous system.

Only a few of the -onium compounds investigated give but one of these effects. The greater number have both actions but in widely varying degree. It has, therefore, been impossible heretofore to bring out any very definite relationship between structure and the tendency to give on the one hand a stimulating nicotine effect and on the other the muscarine effect. It was previously found[4e] that betaine esters (the trimethyl compound) have an intense muscarine action and a moderate stimulating nicotine action. In this series of homologs the triethyl and the tripropyl betaine esters are substantially devoid of either of these actions. The tributyl and, to a greater extent, the triamyl, betaine ester has a very intense stimulating nicotine action but no muscarine action. It would seem, then, that these higher alkyl amine groups have no effect on the inhibitory nerve endings to the heart, but that they do act on the ganglion cells very intensely. This affords a striking case of compounds having similar gross structure (-onium) and similar chemical properties exhibiting a different but highly selective action on the nervous system.

Since Hunt[4f] had found that the substitution of a benzyl group for one of the methyl groups in tetramethylammonium salts seemed to increase the muscarine action, it was thought desirable to test similar substitutions in betaine esters. Several of these were, therefore, prepared. Contrary to the foregoing, it[4k] was found that the substitution of one methyl by one benzyl group lowered the activity in the case of the ethyl esters by

[4] Hunt and co-workers, (a) *Hygienic Lab. Bull.*, No. 73 (1911); (b) *Am. J. Physiol.*, **14,** 197 (1918); (c) *J. Pharmacol.*, **6,** 477 (1915); (d) *ibid.*, **7,** 301 (1915); (e) *ibid.*, **25,** 315 (1925); (f) *ibid.*, **28,** 367, (g) **29,** 17 (1926); (h) *ibid.*, **35,** 75, (i) 99 (1929); *ibid.*, **37,** (j) 177, (k) 309 (1929).

about fifty times and that the introduction of a second benzyl group further greatly diminished both the muscarine and stimulating nicotine action.

Three of the higher homologs of betaine were prepared. As was to be expected these showed marked inactivity.[4k] The inactivity of the betaines has been discussed.[3g]

## Experimental Part

**Homologs of Betaine and Betaine Esters.**—The esters were prepared by condensing molecular quantities of methyl or ethyl bromoacetate with the corresponding tertiary amine. The reaction mixtures, sometimes mixed with an equal volume of toluene, were allowed to stand at −10 to +60° for from several hours to several days. With the higher homologs of trimethylamine there is a greater tendency to form the tertiary amine hydrohalide at the higher temperatures. The solid products formed were purified by recrystallizing from alcohol or acetone or by fractionally precipitating the alcoholic or acetone solutions with absolute ether. The higher homologs were surprisingly soluble in alcohol–ether mixtures, much less soluble in acetone–ether mixtures.

The betaines were prepared by the hydrolysis of the corresponding esters. The hydrolysis was brought about by boiling the esters with aqueous hydrobromic acid. The solutions were then evaporated to dryness and the products purified by precipitating either the alcohol or acetone solution with ether. The slight physiological activity Hunt[4k] found for these products when injected in very large amounts was probably due to the presence of very small quantities of the intensely active esters.

TABLE I

MELTING POINTS AND ANALYSES

| -Onium compound | M. p., °C. | Halogen, % Calcd. | Found | |
|---|---|---|---|---|
| $CH_3OOCCH_2N(C_2H_5)_3Br$ | 132 | 31.50 | 31.60 | 31.59 |
| $C_2H_5OOCCH_2N(C_2H_5)_3Br$ | 104 | 29.85 | 29.95 | 29.87 |
| $CH_3OOCCH_2N(n\text{-}C_3H_7)_3Br$ | 138 | 27.02 | 26.80 | 26.97 |
| $C_2H_5OOCCH_2N(n\text{-}C_3H_7)_3Br$ | 134 | 25.80 | 25.87 | 25.77 |
| $CH_3OOCCH_2N(n\text{-}C_4H_9)_3Br$ | 113 | 23.64 | 23.74 | 23.60 |
| $C_2H_5OOCCH_2N(n\text{-}C_4H_9)_3Br$ | 83 | 22.72 | 22.68 | 22.65 |
| $C_2H_5OOCCH_2N(iso\text{-}C_5H_{11})_3Br$ | 99.5 | 20.28 | 20.37 | 20.47 |
| $C_6H_5HNOCCH_2N(iso\text{-}C_5H_{11})_3Br$ | 169 | 18.12 | 18.00 | 17.91 |
| $CH_3OOCCH_2N(CH_3)_2C_6H_5Br$ | 99 | 29.26 | 29.27 | 29.20 |
| $CH_3OOCCH_2N(CH_3)_2CH_2C_6H_5Br$ | 151 | 27.74 | 27.61 | 27.65 |
| $C_2H_5OOCCH_2N(CH_3)_2CH_2C_6H_5Br$ | 114.5 | 26.49 | 26.55 | 26.58 |
| $CH_3OOCCH_2N(CH_2C_6H_5)_2CH_3Br$ | 128 | 21.97 | 21.93 | 22.03 |
| $C_2H_5OOCCH_2N(CH_2C_6H_5)_2CH_3Br$ | 148 | 21.13 | 20.86 | 21.03 |
| $HOOCCH_2N(C_2H_5)_3Br$ | 190 | 33.29 | 33.20 | 33.36 |
| $HOOCCH_2N(n\text{-}C_3H_7)_3Br$ | 177 | 28.33 | 28.24 | 28.39 |
| $HOOCCH_2N(iso\text{-}C_5H_{11})_3Br$ | 144 | 21.83 | 21.83 | 21.80 |

## Summary

1. Salts of three of the higher homologs of betaine have been prepared. Hunt has found that they, like betaine itself, are markedly inactive on the autonomic nervous system.

2. A number of esters and one phenylcarbamido derivative of the higher homologs of betaine have been prepared. The physiological activity of these esters, as found by Hunt, affords a striking example of the varying effect of different alkyl groups when combined with nitrogen. The trimethyl compound has an intense muscarine action and a moderate stimulating nicotine action. The triethyl and tripropyl have neither of these effects. The tributyl and to a greater extent the tri-isoamyl ester has a very intense stimulating nicotine-like action and no muscarine action.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

# BASIS FOR THE PHYSIOLOGICAL ACTIVITY OF -ONIUM COMPOUNDS. X. HETEROCYCLIC -ONIUM COMPOUNDS[1,2]

BY R. R. RENSHAW AND E. W. SHAND[3]

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The general problem of determining the basis for the physiological activity of -onium compounds has been discussed in earlier papers.[4] It seemed desirable to continue the work by preparing some of the simple heterocyclic -onium compounds with the reduced or partially reduced pyridine and pyrrole type of ring structures such as occur in the simpler alkaloids, nicotine and arecoline, for the latter, especially, has a very specific and strong action on the autonomic system.

Of the types of compounds so far prepared and investigated, the phenyl ethers of the cholines were outstanding in their activity. For this reason we have confined ourselves in the present work largely to the preparation of the phenyl ethers.

The bases pyrrole, pyrroline, pyrrolidine, 3-hydroxypyridine, and 2- and 3-aminopyridines, were prepared in this Laboratory by the best methods available.

The following procedure was used in the preparation of these -onium compounds. Somewhat more than two molar equivalents of the secondary

[1] This problem is being carried out in coöperation with Dr. Reid Hunt of the Harvard Medical School. The physiological data are the basis of another series of papers published elsewhere by him.

[2] This paper is constructed from a portion of a thesis presented by Edward W. Shand, June, 1930, for the degree of Doctor of Philosophy at New York University.

[3] The authors wish to express their appreciation to Parke, Davis & Co. for a Fellowship which has made this work possible.

[4] For earlier references see THIS JOURNAL, **53**, 1471 (1932).

bases pyrroline, pyrrolidine and piperidine were condensed with one molar equivalent of phenoxyethyl bromide in alcohol solution by heating for two hours at 70°. The alcohol was then distilled, the residue made alkaline with aqueous potassium hydroxide, and the solution extracted with ether. From the ether extract, after drying, the phenyl ether of the tertiary base was separated from the secondary base by vacuum fractional distillation. The tertiary base was then converted into the quaternary compound by heating in a benzene or acetone solution for varying lengths of time and the resulting salt purified by recrystallization from acetone, chloroform or from butyl alcohol or ethyl alcohol and ether. The ease of alkylation of the phenyl ethers of the tertiary bases differed considerably.

Efforts to obtain esters of β-pyridine sulfonic acid failed, showing that this substance probably forms an unusually stable betaine.

TABLE I

COMPOUNDS PREPARED

| -Onium compound | M. p. (corr.), °C. | Halogen, % Calcd. | Found | |
|---|---|---|---|---|
| $C_6H_{10}{>}NCH_2CH_2OC_6H_5(CH_3)I$[a] | 121.2 | 36.45 | 36.54 | 36.73 |
| $C_5H_{10}{>}NCH_2CH_2OC_6H_5(C_2H_5)Br$[b] | 112–3 | 25.44 | 25.22 | |
| $C_4H_8{>}NCH_2CH_2OC_6H_5(CH_3)I$[c] | 86.5–7.5 | 38.10 | 37.94 | 37.99 |
| $C_4H_6{>}NCH_2CH_2OC_6H_5(CH_3)I$[d] | 119–21 | 38.34 | 38.20 | 38.23 |
| $C_4H_6{>}NCH_2CH_2OC_6H_5(C_2H_5)I$[e] | 97–9 | 36.77 | 36.54 | 36.38 |
| $C_5H_5{>}NCH_2CH_2OC_6H_5Br$[f] | 80–3 | 28.54 | 28.30 | 28.36 |
| $3\text{-}HOC_5H_4{>}NCH_2CH_2OC_6H_5Br$[g] | 126–7 | 26.98 | 26.82 | 26.89 |
| $2\text{-}(NHCOCH_3)\text{-}C_5H_4{>}NCH_3I$[h] | 177 | 45.66 | 45.80 | 46.09 |
| $3\text{-}(NHCOCH_3)\text{-}C_5H_4{>}NCH_3I$[i] | 220–1 | 45.65 | 45.44 | 45.29 |

[a] Thin rectangular plates from alcohol–ether. [b] Condensation nearly complete after two days' heating in benzene at 90°. Recrystallized from absolute butyl alcohol and ether as granular crystals. [c] The β-phenoxyethylpyrrolidine, b. p. 142–146° at 20 mm., condensed readily in benzene by heating for two hours at 70°. [d] β-Phenoxyethylpyrroline, b. p. 154–158° at 18 mm., condensed at once with methyl iodide at room temperature with evolution of heat; feathery aggregates of thin plates from chloroform–benzene. [e] With ethyl iodide the tertiary base condenses very much more slowly than the preceding, the condensation being complete after eight days at room temperature. Granules of ill-defined crystals from alcohol–ether. [f] This condensation required two days' heating at 70° in benzene. [g] The oily product formed after thirty hours' heating in dry toluene at 70° was finally obtained as thick, almost square plates from acetone–ether. [h] This acetaminopyridine methylates slowly with methyl iodide, the reaction being incomplete after twenty-four hours' heating at 90° in a sealed tube. Rectangular plates from alcohol–ether. [i] Long thin rectangular needles from acetone.

## Summary

1. There is here reported the preparation of β-phenoxyethyl derivatives of the following: -methylpiperidinium iodide, -methylpiperidinium bromide, -methylpyrrolidinium iodide, -methylpyrrolinium iodide, -ethylpyrrolinium iodide, -pyridinium bromide, -3-hydroxypyridinium bromide,

and 3-hydroxy-N-phenoxyethylpyridinium bromide, 2- and 3-acetamino-N-methylpyridinium iodides.

2. Hunt has found that these derivatives of pyridine and piperidine in general have no pronounced effect on the autonomic nervous system. The β-phenoxyethyl-N-methylpyrrolidinium iodide, while giving no muscarine effect, produces an intense stimulating nicotine-like action.

NEW YORK CITY

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENTS OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY, AND FROM THE CHIEF MEDICAL EXAMINER'S OFFICE, AND BELLEVUE HOSPITAL, NEW YORK CITY]

# THE ISOLATION OF PURE, ANHYDROUS ETHYL ALCOHOL FROM NON-ALCOHOLIC HUMAN AND ANIMAL TISSUES

BY ALEXANDER O. GETTLER, JOSEPH B. NIEDERL AND A. A. BENEDETTI-PICHLER

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The object of the present communication is to throw light on the question whether traces of ethyl alcohol are present in human and animal tissues. Some of the earlier workers, notably A. and J. Béchamp, Rajewsky, Vitali, Albertoni, M. Nicloux, Landsberg and Stocklasa,[1] claimed that ethyl alcohol is always present in animal tissues in very small traces, while Arnheim and Rosenbaum, Umber and others claimed that it is absent.[2]

One reason why this problem has not been solved to date is because, if alcohol is normally present at all in organs and tissues, its amount is extremely small. We shall show that distillates from organs contain only about 0.0025% of alcohol at the most and that this small amount is mixed with traces of numerous other volatile organic compounds.

Another reason for disagreement among investigators is the fact that there are no specific tests for alcohol in such dilute solutions. Methods based upon physical constants are all unreliable, both because of the extreme dilution and because of the intermixture of other volatile organic substances. The above experimenters applied the Moore, the Schiff or the Nessler reaction to their oxidized tissue distillates; or tested the distillates directly with Lieben's iodoform or with Nicloux's sulfuric acid–chromate reaction.

Because of the non-specificity of these tests, neither group should have made any claims as to the presence or absence of ethyl alcohol in tissues.

[1] (a) A. and J. Béchamp, *Compt. rend.*, **75**, 1830 (1872); **76**, 836 (1873); **89**, 573 (1879); (b) Rajewsky, *Arch. ges. Physiol.*, **2**, 122 (1875); (c) Vitali, *Ann. Chim. Farm.*, [4] **5**, 113 (1887); (d) Albertoni, *ibid.*, **6**, 250 (1887); (e) M. Nicloux, *Compt. rend. acad. sci.*, [10] **3**, 841 (1896); (f) Landsberg, *Z. physiol. Chem.*, **41**, 505 (1904); (g) Stocklasa, *Deut. med. Wochschr.*, **6**, 198 (1904).

[2] Arnheim and Rosenbaum, *Z. physiol. Chem.*, **40**, 220 (1904); Umber, *Z. klin. Med.*, **39**, 12 (1900).

Nevertheless, several of the investigators even went so far as to make quantitative determinations of the unknown volatile substances which are found in all tissue distillates. They determined these volatile substances: (a) as iodoform, (b) by titrating with standard chromic acid, (c) by oxidizing to acid and titrating with standard alkali.

Their results are reported as follows

| | | |
|---|---|---|
| Ford[3] | In animal blood | 0.0057% |
| Nicloux[4] | In entire guinea pig | 0.001% |
| Landsberg[1f] | In rabbit muscle | 0.028–0.038% |
| Maignon[5] | In dog blood | 0.016–0.027% |
| Pringsheim[6] | In entire rat | 0.044% |
| Pringsheim[6] | In rabbit blood | 0.018% |
| Schweisheimer[7] | In human blood | 0.0368% |

The methods used by these experimenters are not specific for ethyl alcohol. It is common knowledge that the iodoform reaction is given by several volatile organic substances. The chromic acid titration method is based on color changes caused by reduction of the chromate; and ethyl alcohol is only one of many volatile organic substances that will reduce chromic acid. The method based on oxidation and subsequent titration of acidity is not specific for ethyl alcohol because all the various alcohols and aldehydes yield acids on oxidation.

Gettler and Tiber[8] have standardized this latter method, and by it have obtained an average yield of 0.00157% of ethyl alcohol from human brains. They state, however, that this value means simply that if alcohol is normally present in human brains, its average amount is 0.00157%.

Taylor reported finding traces of ethyl alcohol in dog muscle and identified the alcohol by making the ethyl *p*-nitrobenzoate derivative.[9]

Since there is no specific test for ethyl alcohol in the minute traces which we expected to find (*e. g.*, 0.015 g.—one-third of a drop—in an entire brain weighing 1500 g.), special micro-chemical methods had to be selected and devised. We planned to (a) isolate the ethyl alcohol in pure, anhydrous form; (b) determine the boiling point of the pure isolated product; (c) determine quantitatively its carbon content; (d) prepare some derivatives from it (*e. g.*, ethyl benzoate and ethyl iodide); and, finally, (e) determine the boiling points of these derivatives.

**The Tissue Distillation.**—The materials used in the experiments were human brains, livers and blood; dogs' brains, livers and blood; and pigs' brains (listed in Table

[3] Ford, *J. Physiol.*, **34,** 430 (1906).
[4] Nicloux, Thése de Paris, 1900.
[5] Maignon, *Compt. rend. acad. sci.*, **140,** 1063 (1905).
[6] Pringsheim, *Biochem. Z.*, **12,** 143 (1908).
[7] Schweisheimer, *Deut. Arch. klin. Med.*, **109,** 271 (1912).
[8] Gettler and Tiber, *Arch. Path. Clin. Med.*, **3,** 75, 218 (1927).
[9] A. E. Taylor, *J. Biol. Chem.*, **15,** 217 (1913).

I). Of the human specimens, only those were selected that had been under observation in the hospital and in which we were positive that no alcohol had been administered, either internally as beverage or medicine, or externally by rubbing, for at least fifteen days before death. The blood was taken from laboratory workers who never drank alcoholic beverages.

The dogs had been kept in cages for two months and fed nothing but lean meat and water. The pigs' brains had been removed as soon as the animals were killed and sent directly from the slaughter house to the laboratory, where work was commenced immediately.

As soon as the tissues were removed from the body, they were sealed in clean glass containers and kept in the refrigerator until they were ice-cold. Then they were ground up and divided into 500-g. portions, each of which was placed in a one-liter flask with 300 cc. of water. This mixture was subjected to steam distillation, using a long, well cooled condenser with an adapter adjusted to dip into a little ice-cold water in a receiver that was packed in ice.

The distillation was continued on each 500-g. portion until 500 cc. of distillate had been collected; the three 500-cc. distillates from the same liver or brain were then combined for the isolation experiments. One composite sample was made of all the 500-cc. distillates from ten human livers; in the case of dogs' livers and brains, and human blood, where the original material weighed considerably less than 500 g., smaller apparatus was used and proportionately smaller distillates were collected.

The 1500 cc. of steam distillates was then subjected to fractional distillation. It must be pointed out that we were here working with very large volumes of extremely dilute solutions. If alcohol was present at all, these distillates contained only about 0.001% of ethyl alcohol. In our preliminary studies on such dilute alcohol solutions, it was found that the usual distilling flasks could not be used. We found that there is an appreciable loss of alcohol due to absorption by the rubber or cork stoppers and also by some of the alcohol being held back in the dead spaces above the exit tube of the flask and within the top of the condenser. We, therefore, devised entirely new distilling flasks as shown in Fig. 1. The condenser, flask and filling tube are in one piece, thus excluding all stoppers and dead spaces. Four sizes of these flasks, 1000, 500, 100 and 60 cc., were used in the fractional distillations.

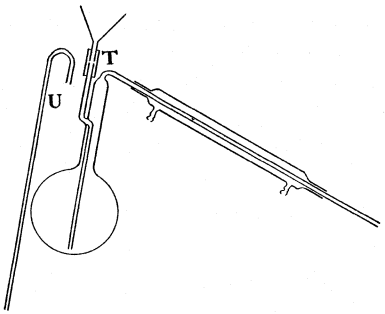


Fig. 1.—Distilling condensing apparatus (in one piece) (according to Gettler and Benedetti-Pichler): T, funnel for filling flask; U, siphon for emptying flask.

It was also important to know how long the distillations had to be continued in order to recover all the alcohol from such dilute solutions. From the work of E. Donitz, M. Nicloux and L. Bandner, M. J. Stritar, and our own experiments, we concluded that with very dilute (0.002%) alcohol solutions, if 40% by volume is distilled, all the alcohol is recovered in the distillate.[10]

In the first distillation the tissue steam distillates were acidified with sulfuric acid to keep back all volatile organic bases; 600 cc. was collected. For the second distillation it was made alkaline with sodium carbonate to keep back all volatile organic acids;

[10] E. Donitz, *Märker-Delbrück, Spiritus-Fabrikation*, p. 694 (1908); M. Nicloux and L. Bandner, *Z. anal. Chem.*, **38**, 256 (1899); M. J. Stritar, *Z. physiol. Chem.*, **50**, 24 (1906).

240 cc. was collected. The third distillation was carried out in neutral reaction; 100 cc. was collected. To these 100 cc. of distillate, freshly prepared silver oxide was added, corked, well shaken and allowed to stand for about one week. This treatment removed all aldehydes by converting them to acids, the latter being fixed as silver salts. Without filtering, this mixture was then distilled; 40 cc. was collected. Aliquot portions of the distillate were used for the quantitative determination of the alcohol, as later described. For the isolation of the alcohol, two further fractional distillations were performed, collecting 16 and 5 cc., respectively.

**Fractional Distillation with Special Rectification Flasks.**—Any further attempts fractionally to distil the 5-cc. distillates obtained above were hopeless, for, if 40% of the 5 cc. were distilled, only 2 cc. would be collected. The alcohol adhering to the large surface of the condenser would mean an appreciable loss of alcohol and it was obvious that rinsing the condenser would be out of the question when trying to concentrate alcohol.

Since we found that most of the alcohol comes over in the first ring of condensate and since we needed a distilling apparatus with condensing surface at a minimum, we devised what we have called the *Rectification Flask* (Fig. 2). With this apparatus we can obtain a very high concentration of alcohol with relatively little technique.

The 5 cc. of concentrated distillate obtained above was transferred to the rectification flask. A small amount of zinc dust was added, to prevent bumping and insure slow but regular boiling. To insure that the upper part of the flask would be absolutely dry inside, the section bd was carefully heated with a small Bunsen flame. When this part of the tube had again cooled to room temperature, a narrow strip of wet filter paper was wrapped around d, to help to keep this part cool.

The distillation was now started by heating the bulb of the flask with a small flame, the temperature being raised slowly and evenly. A ring of condensate rose slowly in the stem of the flask. The moment this passed the knee c, the flame was quickly removed. The ring of condensate collected at d. It was immediately sucked up into a capillary tube, sealed in at both ends and reserved for further work. The whole apparatus was allowed to cool at room temperature and the operation was repeated until several drop fractions had been collected in the same manner.

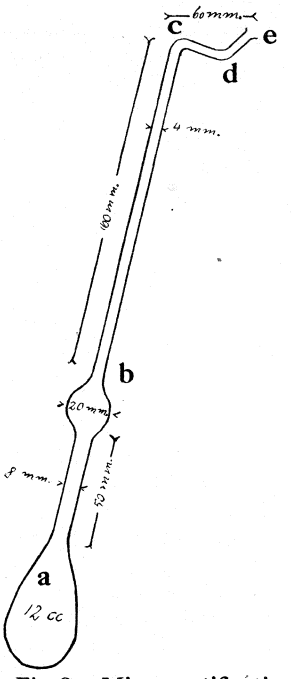


Fig. 2.—Micro-rectification flask (according to Gettler and Bennedetti-Pichler).

The boiling points[11] of the eight fractions of one set of experiments (all other sets gave similar values) were 74, 75, 75.6, 77, 79.8, 80.5, 82.4, 84.4°, respectively, indicating, first, that some liquid was present in the first three fractions, which had a much lower boiling point than ethyl alcohol; second, if ethyl alcohol were present in fractions 4, 5 and 6, it had been obtained in quite high concentration by a single rectification. The lower boiling liquid distilling in the first three fractions was found to be acetone. It was identified by (a) odor, (b) nitroprusside test, (c) conversion into crystals of *o*-nitrophenylhydrazone.

**The Micro Drying of the Rectified Liquids.**—The fractions boiling below 81° were

[11] All boiling point determinations in this work were done by F. Emich's micro method. Emich, *Monatsh.*, **38**, 219 (1917).

combined and transferred to capillary tubes shown in Fig. 3. The bulbs of the tubes were previously filled with a relatively large amount of finely granulated calcium oxide or anhydrous copper sulfate. The capillary was centrifuged to force the liquid into the bulb. The open end was sealed and the tube placed in a boiling water-bath for five minutes. It was again centrifuged to bring the liquid into contact with the dehydrating agent, and then allowed to stand for three days at room temperature.

The bulb of the sealed capillary was then placed in the cavity of an aluminum heating block (Fig. 3, c); the latter was heated to 95° and kept constant for five minutes. The alcohol distilled from the bulb and appeared as a condensate on the walls of the capillary outside of the heating block. The tube was removed from the block, cut in two at the middle, and the part holding the condensate was centrifuged to force the alcohol to the sealed end (Fig. 3, d, e). These dried droplets were fractionally distilled as follows.

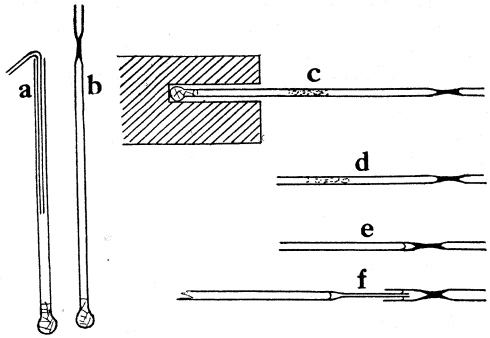


Fig. 3.—Drying tubes, drying block, and boiling point capillaries.

**Fractionating with Emich's Micro Distilling Tube.**—The dry droplets of liquid obtained were transferred to an Emich micro distilling tube and fractionally distilled. Six to eight fractions were usually obtained and the boiling point of each was determined. By this means the acetone was separated from the liquid boiling between 77 and 79°.[12]

The rise of the droplets in the capillary tubes during the micro boiling determinations on pure anhydrous ethyl alcohol behaved exactly as did the liquid (boiling between 77 and 79°) isolated from tissues, and both gave similar values, proving that the isolated liquid was ethyl alcohol.

**The Micro Determination of the Carbon Content of Isolated Ethyl Alcohol.**—For the determination of the carbon content of the ethyl alcohol isolated from tissues, we used the purified and perfectly dried fractions that boiled between 78 and 79°. The quantitative analysis by Pregl's micro method[13] showed that the droplets of liquid isolated from tissues which boil at 78 to 79° contain 51.8% carbon.

The theoretical carbon content of closely related substances is as follows

| | | | |
|---|---|---|---|
| Methyl alcohol | 37.5% | Propyl alcohol | 60.0% |
| Ethyl alcohol | 52.1% | Acetone | 62.1% |

Since the pure liquid that we isolated from tissues (b. p. 78 to 79°) had a carbon content of 51.8%, it served to prove that the isolated material was ethyl alcohol.

**Identification of Isolated Material as Ethyl Alcohol by Conversion to Ethyl Benzoate.**—To prepare the benzoate derivative, we used the fractions boiling between 77 and 80°. Ten to 20 mg. of the alcohol was placed in a glass tube measuring 10 cm. in length and 3 mm. in its inner diameter, and sealed at one end. An equal amount of benzoyl chloride was added, and the liquids were mixed by means of a bead on the end of a fine glass thread. The tube was then corked and allowed to stand overnight.

The next day enough sodium bicarbonate was added to neutralize all the benzoic

[12] Emich, "Lehrbuch Microchemie," 2d ed., Munich, 1926.

[13] Pregl, "Quantitative Organic Micro Analysis," 2d ed., P. Blakiston's Sons Co., Philadelphia, Pa., 1930.

acid and hydrochloric acid that had been formed, and a few drops of water were added. Most of the sodium salts remained undissolved. The contents were stirred occasionally with the glass bead until the odor of benzoyl chloride disappeared (usually three to six hours). Enough ether was then added to form a 3-cm. layer; the tube was corked and well shaken, and finally centrifuged. The supernatant ether layer was transferred to another tube of the same type by means of a capillary siphon, and enough freshly dehydrated potassium carbonate was added to form a layer 1 cm. deep. After these two substances were well mixed with the glass bead, the tube was corked and allowed to stand overnight.

An Emich micro fractionating tube, containing a small layer of asbestos, was freed from moisture by heating it in a small Bunsen flame. As soon as it was cold again, the ether layer described above was transferred to it in several separate portions by means of a capillary tube which placed the liquid right in the asbestos at the bottom. After the introduction of each portion, the ether was evaporated by resting the fractionating tube on a lighted electric bulb. The ester was thus collected quantitatively in the asbestos of the fractionating tube. The tube was finally heated gently above a micro burner, to remove the last traces of ether, but care was taken not to distil any of the ester.

The ether-free ester was fractionally distilled from the asbestos. The middle and end fractions were redistilled in the same manner, and the last three fractions were used

TABLE I

TISSUES USED FOR THE ISOLATION AND IDENTIFICATION OF ETHYL ALCOHOL

| No. | Tissue | Weight, g. | B. p. of the isolated EtOH, °C. | B. p. of the benzoate derivatives, °C. | B. p. of the iodide derivatives, °C. | Zeisel alkoxy reaction |
|---|---|---|---|---|---|---|
| 1 | 1 Human brain | 1800 | 79 | 182–204 | 71.5 | Positive |
| 2 | 4 Human brains | 6300 | 77.9 | 190–208 | 71.0 | Positive |
| 3 | 1 Human brain | 1265 | 78.1 | 185–205 | 68.0 | Positive |
| 4 | 1 Human brain | 1225 | 77.8 | 180–205 | 69 | Positive |
| 5 | 1 Human brain | 1500 | 78.2 | 188–207 | 71.7 | Positive |
| 6 | 10 Human livers | 17000 | 78 | 190–206 | .. | Positive |
| 7 | 1 Human liver | 1225 | 78.2 | 180–204 | 72.5 | Positive |
| 8 | 1 Human liver | 1000 | 78.1 | 186–205 | 71.9 | Positive |
| 9 | 1 Human liver | 1180 | 77.8 | 190–205 | 70.2 | Positive |
| 10 | 1 Human liver | 1290 | 78.2 | 189–207 | 70.8 | Positive |
| 11 | 1 Human liver | 950 | 77 | 185–204 | 71.8 | Positive |
| 12 | 1 Human blood | 25 | 77.8 | 182–201 | .. | Positive |
| 13 | 3 Human blood | 80 | 78.1 | 175–190 | 69.9 | Positive |
| 14 | 3 Human blood | 90 | 77.6 | 185–204 | 71.8 | Positive |
| 15 | 1 Human blood | 150 | 78.7 | 191–207 | 72.1 | Positive |
| 16 | 1 Human blood | 45 | 77.9 | 188–206 | 71.9 | Positive |
| 17 | 2 Dog brains | 125 | 77.1 | ..... | 71.5 | Positive |
| 18 | 2 Dog brains | 155 | 77.6 | 182–203 | .. | Positive |
| 19 | 2 Dog brains | 145 | 77.5 | 185–204 | 70.9 | Positive |
| 20 | 2 Dog livers | 410 | 79.8 | ..... | .. | Positive |
| 21 | 2 Dog livers | 520 | 77.6 | 183–203 | .. | Positive |
| 22 | 2 Dog livers | 440 | 78.9 | ..... | 71.8 | Positive |
| 23 | 2 Dogs' blood | 350 | 77 | 180–203 | 72.0 | Positive |
| 24 | 2 Dogs' blood | 420 | 78 | 181–202 | 71.5 | Positive |
| 25 | 2 Dogs' blood | 490 | 77.2 | 184–205 | 71.9 | Positive |
| 26 | 300 Pigs' brains | 28000 | .. | ..... | 54 | Positive |
| 27 | 300 Pigs' brains | 28200 | 78.2 | 189–206 | 72.0 | Positive |

for the micro boiling point determinations. The boiling points of the benzoate derivatives are given in Table I.

Although pure ethyl benzoate boils at 212°, it was found by the micro boiling point method that the values for the pure product actually range from 205 to 213°. Ethyl benzoate made from pure alcohol boiled at 190 to 206° and 195 to 208°. Since these figures compare so favorably with those of the benzoate made from tissue distillates, they prove that the derivative is ethyl benzoate. This ester was further identified by its odor and by its insolubility in water.

The production of ethyl benzoate corroborates that the liquid isolated from the tissues was ethyl alcohol.

**The Identification of Isolated Material as Ethyl Alcohol by Conversion to Ethyl Iodide.**—The preparation of the iodide derivative is based on the interaction of ethyl alcohol and hydriodic acid. The apparatus and method used was exactly the same as shown in Fig. 4 and described under the quantitative determination (to follow), except that the receiver was empty and was packed in a mixture of acetone and solid carbon dioxide in a Dewar flask.

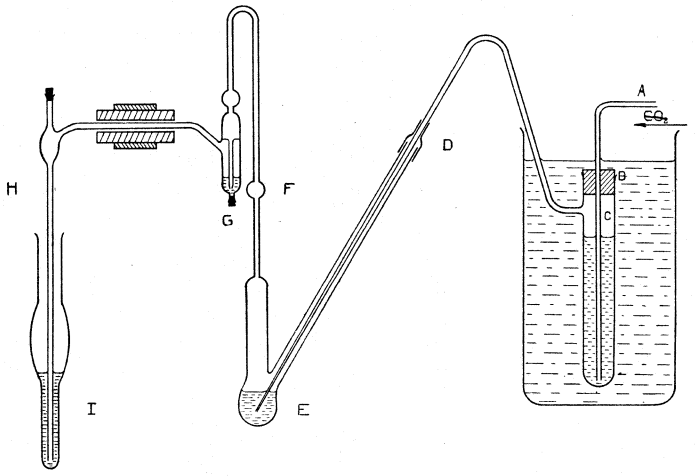


Fig. 4.—Pregl's ethoxy apparatus (as modified by Gettler and Niederl): A, carbon dioxide inlet tube; B, stopper; C, side-arm test-tube; D, inlet tube; E, hydriodic acid bulb; F, condenser; G, washer; H, capillary outlet; I, receiver.

Five cc. of concentrated aqueous distillate from tissues was placed in the side-arm test-tube. Soon after starting the experiment, ice was noticed in the receiver (kept at −80° by the carbon dioxide–acetone mixture), but the operation was continued for thirty to fifty minutes, until a heavy liquid and a yellowish-white solid had formed. The receiver was then removed from the apparatus and allowed to attain room temperature, the solid melted and settled on top of a few drops of a heavy oil; the two liquids were not miscible.

The top layer, which was found to be water, was drawn off by means of a capillary siphon and the heavy oil was transferred by another capillary siphon to a micro centrifuge tube. A drop of distilled water was added and the mixture was stirred by a glass bead on a fine glass thread. By centrifuging the mixture a clear separation was effected and the water layer on top was then drawn off. This washing procedure was repeated several times.

For the identification of the ethyl iodide, the boiling point was determined. The results are listed in Table I.

The boiling point of absolutely pure ethyl iodide is 72.3°. The figures obtained with our product are close enough to this to indicate that the isolated compound is ethyl iodide. The uniformly lower boiling points may be due to the persistent presence of some slight impurities.

**Quantitative Determination of the Alcohol in Tissues.**—For our quantitative micro method we essentially followed Pregl's adaptation of Zeisel's reaction for alkoxy groups. This is based on the formation of ethyl iodide by the direct interaction of ethyl alcohol and hydriodic acid and the subsequent quantitative determination of the silver iodide precipitated when the ethyl iodide is absorbed in an alcoholic silver nitrate solution. We have, however, made some constructive changes in both the apparatus and the method so that they are now applicable to extremely dilute ethyl alcohol solutions (0.02% and less), and have standardized the method for a total alcohol content of 0.1 mg. to 1 mg.[13,14]

The apparatus consists of a Kipp generator for the production of carbon dioxide, an especially constructed side-arm test-tube for the solution to be tested, Pregl's micro ethoxy apparatus, and a receiver containing an alcoholic silver nitrate solution,[15] arranged as shown in Fig. 4.

Holding the micro ethoxy apparatus in a horizontal position, about 1 cc. each of 5% solutions of sodium thiosulfate and cadmium sulfate were introduced into the washer g by a capillary pipet. The purpose of the sodium thiosulfate is to absorb any free iodine that might be liberated during the course of the experiment; the cadmium sulfate, to remove hydrogen sulfide or any other volatile sulfides. The opening of g was then tightly closed with a tiny cork, it was inverted to its proper position, and 1.5 cc. of hydriodic acid, sp. gr. 1.70 (Merck's special), was placed in the bulb e. Five grams of anhydrous potassium carbonate was placed in the side-arm test-tube, to lower the vapor pressure of the water and to facilitate the separation of the alcohol in the liquid to be tested.

Five cc. of concentrated tissue distillate was placed in the side-arm test-tube. When all connections of apparatus were made, the latter was heated in a water-bath to facilitate the volatilization of the alcohol present. The outlet from the Kipp generator was opened just far enough to allow carbon dioxide to pass in at the rate of two or three bubbles a second; then the hydriodic acid in e was heated to slow boiling. The process was stopped when no more precipitation occurred in the receiver containing the alcoholic silver nitrate.

One cc. of water and five drops of nitric acid were added to the precipitated addition compound ($AgI \cdot 2AgNO_3$) in the receiver, and the whole was heated in a boiling water-bath. This hydrolyzed the addition compound, leaving the silver iodide in a nicely precipitated, filterable form. This precipitate was quantitatively transferred to a micro halogen filter tube (prepared and filled according to Pregl's method), and washed with alcohol. The tube was then placed in a micro heating block and dried at 120° in vacuum, using a suitable air filter. When completely dry (about ten minutes) and at constant weight the tube was weighed on a micro chemical balance to within 0.001 mg.[13]

Each milligram of silver iodide produced by this reaction represents 0.196 mg. of

[14] S. Zeisel, *Monatsh.*, **6**, 989 (1885); S. Zeisel and R. Fanto, *Z. landw. Versuchsw.*, **5**, 729 (1902); *Z. anal. Chem.*, **72**, 549 (1903).

[15] Twenty grams of silver nitrate dissolved in 500 g. of 95% alcohol; solution boiled three to four hours under reflux on water-bath. Reduced silver separates in finely divided form; after standing for two days, supernatant liquid decanted into dark stock bottle.

ethyl alcohol. Under the experimental conditions of this reaction, recovery is not complete and a correction value must be figured in the calculations. Our control experiments indicated a correction of 0.273; therefore (mg. of AgI + 0.273) × 0.196 = mg. of ethyl alcohol in 5 cc. of distillate analyzed.

The tissues that were used in these determinations and the results obtained are listed in Table II. The average content of ethyl alcohol in these tissues that were known to be non-alcoholic is as follows: human brain, 0.0004%; human liver, 0.00256%; human blood, 0.004%; dog brain, 0.0003%; dog liver, 0.0007%; dog blood, 0.0013%; pigs' brains, 0.00007%.

TABLE II

AMOUNT OF ETHYL ALCOHOL PRESENT IN NORMAL TISSUES

| No. | Specimens | Tissues used, g. | Ethyl alcohol present in mg. per 100 g. | Per cent. |
|---|---|---|---|---|
| 1 | 1 Human brain | 1800 | 2.72 | 0.00027 |
| 2 | 4 Human brains[a] | 6300 | 3.27 | .00033 |
| 3 | 1 Human brain | 1265 | 5.45 | .00055 |
| 4 | 1 Human brain | 1225 | 4.35 | .00044 |
| 5 | 10 Human livers[a] | 17000 | 7.56 | .00076 |
| 6 | 1 Human liver | 1225 | 25.05 | .00250 |
| 7 | 1 Human liver | 1000 | 39.90 | .00400 |
| 8 | 1 Human liver | 1180 | 22.06 | .00220 |
| 9 | 1 Human liver | 1290 | 55.35 | .00550 |
| 10 | 1 Human liver | 950 | 4.84 | .00040 |
| 11 | 1 Human blood | 25 | 45.31 | .0045 |
| 12 | 2 Human blood[a] | 55 | 47.1 | .0047 |
| 13 | 1 Human blood | 30 | 38.2 | .0038 |
| 14 | 1 Human blood | 25 | 32.4 | .0032 |
| 15 | 300 Pigs' brains[a] | 28000 | 0.68 | .00007 |
| 16 | 2 Dogs' brains[a] | 125 | 3.30 | .0003 |
| 17 | 2 Dogs' livers[a] | 410 | 6.90 | .0007 |
| 18 | 2 Dogs' blood[a] | 350 | 13.70 | .0013 |

[a] Composite samples.

Special experiments were made to determine whether there might be any change in the alcohol content of tissues after removal from the body. In one of these approximately equal amounts of blood from three non-drinking persons were combined into one 110-cc. sample. One half of this sample was analyzed at once for alcohol content; the other half was kept in the refrigerator overnight and then analyzed. The results were 0.0050% and 0.0044%, respectively, indicating that the alcohol must have been present when the blood was taken from the body, not formed after removal.

**Acknowledgment.**—We wish to thank Mr. Pierre du Pont and Doctor Samuel Lambert for the interest they have taken in this work.

## Summary

Apparatus has been devised for the isolation of pure, anhydrous ethyl alcohol from extremely dilute solutions (0.0025% or less) as found in tissues: (a) distillation flask with condenser and filling tube, all in one piece, no corks needed, thus obviating the loss of volatile matter in stoppers and dead spaces; (b) a rectification flask in which the condensing surfaces are

kept at a minimum. A single distillation yields a few drops of very high proof alcohol, b. p. 78 to 79°.

The isolated alcohol was dried by calcium oxide or anhydrous copper sulfate in one end of a sealed capillary; it was then distilled into the other end of the same sealed tube by means of a heated aluminum block.

The perfectly dry material was transferred from the capillary to an Emich micro distilling tube and fractionally distilled. With this tube even fractions of a drop can be distilled, and by this means the acetone which is always present in tissues was separated from the ethyl alcohol. (Other volatile substances, such as aldehydes, ketones, organic acids and bases, were removed at various other steps during the procedure.)

Micro boiling point determinations were made on the pure isolated ethyl alcohol for purposes of identification.

The ethyl alcohol was further identified by its solubility and by the quantitative determination of its carbon content.

From the ethyl alcohol isolated from tissues, using a micro technique, the ethyl benzoate derivative was prepared; it was identified by its boiling point, solubility and odor.

From the ethyl alcohol isolated from tissues, using a micro technique based on Pregl's alkoxy apparatus, the ethyl iodide derivative was prepared; it was identified by its boiling point and solubility.

The amounts of alcohol normally present in tissues were determined by a modification of Pregl's micro method, using the Zeisel reaction.

The average amount of ethyl alcohol present normally in body tissues was found as follows: human brain, 0.0004%; human liver, 0.00256%; human blood, 0.004%; dog brain, 0.003%; dog liver, 0.0007%; dog blood, 0.0013%; pig brain, 0.00007%.

**Conclusion.**—Pure anhydrous ethyl alcohol was isolated and identified from the brain, blood and liver of non-alcoholic humans, dogs and pigs.

NEW YORK CITY, N. Y.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

# HEPTAMETHYLSUCROSE: A CORRECTION

BY JAMES COLQUHOUN IRVINE AND ERIC THOMAS STILLER

RECEIVED SEPTEMBER 28, 1931 PUBLISHED APRIL 6, 1932

According to published accounts,[1] when sucrose is methylated by methyl sulfate and alkali the product, after one treatment with the reagents, consists essentially of a heptamethylsucrose in which four methyl groups are present in the fructose half of the molecule and three in the glucose component. This reaction was, in fact, utilized by Haworth as the source of tetramethyl-γ-fructose in the constitutional study of the fructose residue in sucrose.

In the course of further work now in progress in this Laboratory on the structure of sucrose it has been necessary, as a side issue, to examine the methylated derivatives of the disaccharide in detail and to direct special attention to the "heptamethyl sucrose" described by Haworth. As a result of a prolonged research in which advantage was taken of improved methods for separating and identifying methylated sugars we find that the methylation of sucrose is far from being the simple reaction claimed by Haworth. Under the conditions described by him, the methylation of sucrose yields a complex mixture of compounds boiling at approximately a constant temperature and giving the correct analytical figures only as a result of numerous compensations. As this partially methylated sucrose is a sirup and, so far, has yielded no crystalline derivatives, vacuum distillation offers the only method of isolation; but the process is ineffective as a means of separating the mixture of compounds into its components and the lack of uniformity was revealed only when the material was hydrolyzed and the scission sugars carefully separated and identified. This we have done, keeping a record of the weight of each constituent, which is expressed in percentages of the weight of "heptamethyl sucrose" used. We find that, in addition to tetramethyl-γ-fructose (45%), the hydrolysis sugars contained 15% of tetramethylglucose and this result, making allowance for the amount of trimethyl-γ-fructose which was also present, shows that *octa*methylsucrose formed at least 27.5% of the original material. Partially methylated hexoses, belonging to both the glucose and fructose series, were also produced in the hydrolysis and amounted approximately to 40%, made up of 14% of mono- and di-methylglucoses together with 25% of various trimethylhexoses. The latter were not homogeneous in type, as at least 8% of trimethyl-γ-hexoses was present along with three, and possibly four, isomeric trimethylglucoses. In short, not more than

[1] Haworth, *J. Chem. Soc.*, **107**, 12 (1915); **117**, 199 (1920); Haworth and Mitchell, *ibid.*, **123**, 301 (1923).

one-third of the original methylated sucrose consisted of heptamethylsucrose and even this is not a chemical individual but a mixture of at least four isomerides.

The combined results give a clue to the order in which the methyl groups enter the sucrose molecule. Evidently the fructose component is substituted preferentially as the amount of tetramethyl-γ-fructose greatly exceeds that of tetramethylglucose and no ketoses with a lower methoxyl content than trimethylfructose were detected. Nevertheless, before the whole of the fructose residues are fully substituted, some of the glucose residues likewise undergo complete methylation while in the remainder methyl groups are scattered throughout the glucose chain. Positions 2,3,6-, 2,4,6-, and 2,3,4- in the glucose component definitely take part in the partial substitution and possibly also 2,3,5- as is shown by the isolation of the corresponding trimethylglucoses. Similarly 2,3-dimethylglucose was also identified with certainty in the lower methylated hexoses. The preference for positions 2 and 3 is interesting, but the possibility that the sucrose molecule may undergo methylation in position 5 of the glucose chain is disconcerting. The amount of 2,3,5-trimethylglucose detected was small, but nevertheless at least 5% of the total trimethylglucose consisted of this sugar[2] and its constitution is evident from the following properties. The compound was a reducing sugar and position 1 was therefore unmethylated. Position 4 was likewise unmethylated as the sugar gave an authentic γ-methylglucoside and not a semi-acetal when condensed with methyl alcohol under conditions favorable to γ-glucoside formation; position 6 was also unmethylated as the *p*-toluenesulfonyl derivative was convertible into the corresponding iodo derivative, a transformation which in the glucose series is restricted to the primary alcohol group.[3]

It is not inconceivable that this 2,3,5-trimethylglucose originated in partial hydrolysis of the sucrose molecule during methylation, although all experience is opposed to the idea that under such circumstances glucose reverts to the γ-form. There remains the more disquieting possibility that methylation is accompanied to some extent by a change in the position of the internal oxygen ring in a sugar. Although the validity of the methylation method as a means of determining structure has not escaped challenge, the evidence hitherto offered in criticism of the process has not been convincing, but it must be admitted that the case now presented opens up grave possibilities. If the oxygen ring alters in the glucose component

[2] The possibility that the sugar referred to may be 1,3,4-trimethylfructose has not been overlooked. The properties of the compound as displayed in the method of isolation are not strictly in accordance with either possibility, but as the sugar in the form of its γ-methylglucoside survived a treatment known to decompose the corresponding fructosides, the combined evidence favors the view that it is a derivative of glucose rather than of fructose.

[3] Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932).

of sucrose even to the extent of 5%, it may conceivably do so to a greater extent in the more reactive fructose half of the sucrose molecule, in which case the constitution of the disaccharide may require revision. The present formula accounts for the known properties of the disaccharide so far as these can be interpreted in terms of structure and its value is not necessarily impaired by the repeated failures to synthesize sucrose on the lines of the formula. But it is evident that an unsuspected element of uncertainty attends the methylation process and this may lead ultimately to further revision of the structures now assigned to many carbohydrates.

In order to economize description the general principles underlying the experimental methods we employed are summarized so as to indicate the reasons for the various operations.

1. Extraction of an aqueous solution of methylated hexoses with chloroform removes compounds containing four or five methyl groups in each chain of six carbon atoms (*e. g.*, tetramethyl reducing hexoses, the corresponding methylhexosides and also trimethylmethylhexosides).

2. Compounds containing three methyl groups in the hexose chain (*e. g.*, trimethylglucose or dimethylmethylglucoside) are extracted by chloroform from an aqueous solution saturated with potassium carbonate.

3. The above processes used in conjunction with the fact that an additional methyl group can be introduced into a sugar by conversion into the corresponding methylglucoside or, conversely, a methyl group can be eliminated from a methylglucoside by hydrolysis admits of a sharp separation of tetra-, tri-, di- and monomethylhexoses, when $\gamma$-derivatives are absent.

4. Condensation of mixed methylated sugars with methyl alcohol in the cold converts components which are capable of reacting in the $\gamma$-form into the corresponding $\gamma$-methylglucosides. When a sugar fails to form a $\gamma$-glucoside, position 4 must be methylated and when it is incapable of normal methylglucoside formation position 5 must be similarly substituted.

5. Mixtures of glucosides consisting partly of $\gamma$-forms and partly of normal forms can be separated into their respective classes by graded hydrolysis with $N/100$ hydrochloric acid which affects only the $\gamma$-isomerides.

6. When mixtures contain methylated reducing hexoses and also methylated glucosides, the former can be destroyed without damage to the latter by boiling with aqueous alkali.

7. When position 6 in the glucose series is unmethylated, the primary alcohol group can be substituted by the *p*-toluenesulfonyl residue which, in turn, is replaceable by iodine. The halogen can be removed quantitatively and estimated, thus giving the content, in a mixture, of any sugars unsubstituted in the terminal position.

## Experimental

All evaporations and distillations were conducted under diminished pressure, all hydrolyses and condensations were followed by polarimetric observations, and the composition of each compound was verified by analysis or by comparison with standard specimens. The validity of each process was verified by means of control experiments, the account of which is omitted from the text.

Pure sucrose was methylated exactly as described by Haworth[1] and 100 g. of the product, which gave analytical figures agreeing for a heptamethylsucrose, was hydrolyzed by $N/100$ hydrochloric acid. On extraction from aqueous solution with chloroform the tetramethylhexoses were separated from lower methylated hexoses.

**Tetramethylhexoses.**—(Weight, 54 g.) The mixed sugars were condensed with cold methyl alcohol under conditions which give tetramethyl-$\gamma$-methylfructoside while tetramethylglucose remains unaltered. The latter was destroyed by boiling with alkali, the fructoside (44 g.) recovered, hydrolyzed as usual and the tetramethyl-$\gamma$-fructose (34.4 g.) isolated at 117–119° (0.05 mm.). Found: $n_D$ 1.4533; $[\alpha]_D$ +30.7° in water for $c = 1.5155$. Control experiments showed that the above methods are effective in separating tetramethyl-$\gamma$-fructose from the stable form of tetramethylglucose.

**Lower Methylated Hexoses.**—(Weight, 38 g.) The mixed sugars, containing both partially methylated glucose and fructose, were condensed with acid methyl alcohol at the boiling point and the products extracted from water by chloroform. The extract (A) then contained trimethylmethylglucosides and trimethyl-$\gamma$-methylfructosides (24 g.) while the aqueous layer (B) retained di- and monomethylmethylglucosides (13.6 g.).

**Treatment of A.**—Regulated hydrolysis with $N/100$ hydrochloric acid converted the $\gamma$-fructosides into trimethyl-$\gamma$-fructose, which was isolated as usual and identified by analysis and specific rotation. The trimethylmethylglucosides which remained unaffected were then boiled with alkali to destroy reducing sugars and ultimately isolated by vacuum distillation (8.4 g.). Hydrolysis of the distillate with 8% hydrochloric acid gave a mixture of trimethylglucoses (6.2 g.) the separation of which is described later.

**Treatment of B.**—The mixture of di- and monomethylmethylglucosides and fructosides was recovered, dissolved in water, saturated with potassium carbonate and extracted with chloroform. Monomethylated methylglucosides remained in the aqueous layer from which 1.8 g. of monomethylmethylglucoside was isolated analytically pure. The chloroform extract contained 10.8 g. of dimethylmethylglucosides which were examined as afterward described.

**Examination of Trimethylglucoses.**—The sirupy product was allowed partially to crystallize. On treatment with dry ether the crystalline trimethylglucose (m. p. 121–123°) noted by Haworth remained. As this sugar was not identical with 2,3,6-, 2,3,4- or 3,4,6-trimethylglucose, specimens of which were available for comparison, it is probably the 2,4,6-isomeride. The sugar dissolved by the ether (14 g.) was condensed with methyl alcohol in the cold and, following the usual procedure, trimethyl-$\gamma$-methylglucoside (5.7 g.) was separated from normal trimethylglucose (8.1 g.) The former on hydrolysis gave, as anticipated, 2,3,6-trimethylglucose on hydrolysis of a sample but a more important result was obtained by conversion of the $\gamma$-glucoside into the corresponding *p*-toluenesulfonate. In this way trimethyl-5-*p*-toluenesulfonyl-$\gamma$-methylglucoside was obtained (5 g.) but the product did not consist exclusively of the 2,3,6-isomeride as when heated in acetone solution with sodium iodide an iodo derivative was formed to the extent of 14%. This was verified by heating in acetonitrile solution with silver nitrate and weighing the silver iodide formed. In view of its origin the parent sugar is unlikely to have been a fructose derivative and this was supported by control experiments, yet it forms a $\gamma$-glucoside and has no methyl group in position 6; it is probably 2,3,5-trimethylglucose.

The trimethylglucose (8.1 g.) left uncombined in the condensation with methyl alcohol were acetylated, treated with hydrogen bromide in glacial acetic acid solution and the product on isolation shaken with methyl alcohol in the presence of silver carbonate. In this way 7.8 g. of a mixture of mono-acetyltrimethyl-β-methylglucosides were obtained and this, after de-acetylation, was distilled in a high vacuum. The trimethyl-β-methylglucosides thus produced (4.6 g.) were treated in the customary manner with *p*-toluenesulfonyl chloride and the product heated at 100° for two hours in acetone solution with sodium iodide; 65% of the material remained as unchanged trimethyl-*p*-toluenesulfonyl-β-methylglucosides, indicating that to this extent position 6 was methylated so that the parent sugar must have been either 2,4,6- or 3,4,6-trimethylglucose or a mixture of both forms. The remainder of the glucoside sulfonate transformed smoothly into 6-iodo-trimethyl-β-methylglucoside, evidence that group 6 was unmethylated and was therefore derived from 2,3,4-trimethylglucose. This was confirmed by heating in acetonitrile solution with silver nitrate, thereby converting the iodo derivative into the corresponding nitrate and thereafter reducing with iron and acetic acid. Extraction of an aqueous solution of the reduced product with chloroform yielded 2,3,4-trimethyl-β-methylglucoside melting after recrystallization from light petroleum at 92–93° and identical with an authentic specimen. The aqueous layer yielded in equal amounts (a) a sirup which was not identified and (b) 1.4 g. of a product crystallizing from alcohol (m. p. 104–105°) which analysis proved to be 3,4,6- or 2,4,6-trimethyl-*p*-toluenesulfonyl-β-methylglucoside.

**Examination of Dimethylglucoses.**—This series of products, obtained in the form of the methylglucosides, was dissolved in water and extracted with chloroform to remove trimethylmethylglucoside (3 g.). The purified dimethylmethylglucoside (8.4 g.) was treated with *p*-toluenesulfonyl chloride giving 10 g. of sulfonated product, the composition of which was established by analysis. After heating in acetone solution with sodium iodide 6-iodo-2,3-dimethylmethylglucoside was isolated and identified but 46% of the dimethyl-di-*p*-toluene-sulfonyl methylglucoside remained unaltered, showing that to this extent position 6 was methylated. The parent sugar was in all probability 2,6-dimethylglucose.

The thanks of the authors are due to the Carnegie Trust for a scholarship which has enabled one of them to take part in the work.

## Summary

1. The "heptamethyl sucrose" described by Haworth in his constitutional study of sucrose is not a homogeneous compound but a complex mixture containing 30% of octamethylsucrose.

2. The nature of the mixture is revealed when the material is hydrolyzed and the scission sugars separated and identified individually.

3. The hydrolysis sugars consist as a minimum of ten compounds, *viz.*: (a) tetramethyl-γ-fructose, 45%, (b) tetramethylglucose, 15%, (c) trimethyl-γ-fructoses, 8%, (d) four isomeric forms of trimethylglucose, 17%, (e) 2,3-dimethylglucose, one other isomeride and monomethylglucoses amounting to 14% of the weight of methylated sucrose used.

4. Evidence has been obtained showing the order in which methyl groups enter the sucrose molecule and that, so far as the glucose component is concerned, this is similar to that in starch.

5. Evidence has also been obtained that the methylation of sucrose may

be accompanied to some extent by alteration in the position of the oxygen ring in the glucose component.

St. Andrews, Scotland

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[Contribution from the Chemical Research Laboratory of the United College of St. Salvator and St. Leonard, University of St. Andrews]

# SYNTHESIS OF 2,3,6-TRIMETHYLGLUCOSE

By James Colquhoun Irvine and Jean Kerr Rutherford

Received September 28, 1931 Published April 6, 1932

2,3,6-Trimethylglucose was first prepared by Denham and Woodhouse[1] who, working in this Laboratory, obtained the sugar by hydrolyzing methylated cellulose; in justice to these workers whose pioneer efforts have been ignored by others, it is advisable to recall that we also owe to them the use of methyl sulfate as a methylating agent applicable to carbohydrates.

Obviously the constitution of 2,3,6-trimethylglucose is of unusual importance as the structural formulas meanwhile assigned to many disaccharides and to all the polysaccharides derived from glucose are based ultimately on the capacity of these particular compounds to be converted into this variety of trimethylglucose. The point is elaborated in a previous paper[2] where it is, however, emphasized that the formation of 2,3,6-trimethylglucose by the hydrolysis of a methylated saccharide is not conclusive evidence of structure as it fails to discriminate between the normal and $\gamma$-types of glucose residues. This much is nevertheless certain—when 2,3,6-trimethylglucose is obtained in a structural study conducted by the methylation method the parent compound must have contained unsubstituted hydroxyl groups in positions 2, 3 and 6; no further conclusions are justifiable.

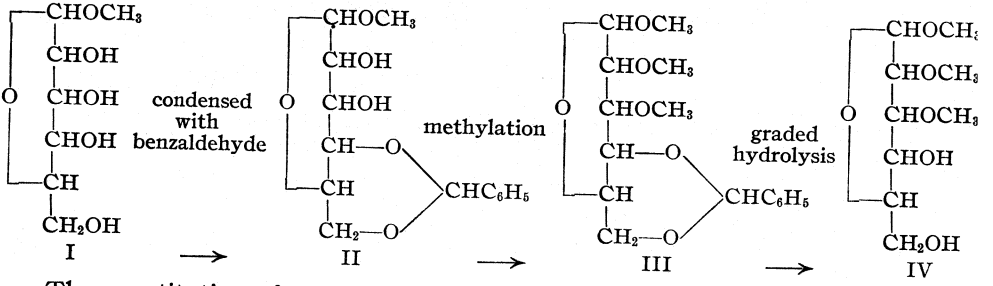
The evidence upon which the constitution of this methylated sugar depends has been accumulated gradually. In the first place Denham and Woodhouse[1] showed that the compound failed to form an osazone and that when converted into the corresponding heptonic lactone a methoxyl group was eliminated. In this way, methyl groups are definitely assigned to positions 2 and 3 in the glucose chain and the proof was completed by Irvine and Hirst,[3] who found that when the sugar was oxidized to a dibasic acid one of the methyl groups was removed and this group must have occupied position 6. Confirmation of the formula was supplied by Irvine and McGlynn,[2] who showed that this particular trimethylglucose could react equally as a normal or as a $\gamma$-sugar, from which it follows that groups 1, 4 and 5 must be unmethylated.

[1] Denham and Woodhouse, *J. Chem. Soc.*, **105**, 2357 (1914).

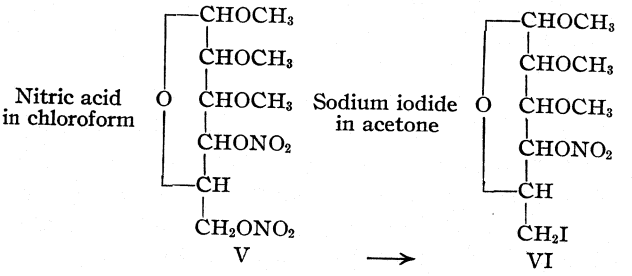
[2] Irvine and McGlynn, This Journal, **54**, 356 (1932).

[3] Irvine and Hirst, *J. Chem. Soc.*, **121**, 1213 (1922).

Although there seemed no reason to doubt the validity of these arguments it was advisable to confirm, by synthetical methods, a constitutional formula upon which so much depends and this we have succeeded in doing. The starting point was $\alpha$-methylglucoside which was converted by improved methods into the 2,3-dimethylmethylglucoside (formula IV) described by Irvine and Scott[4]

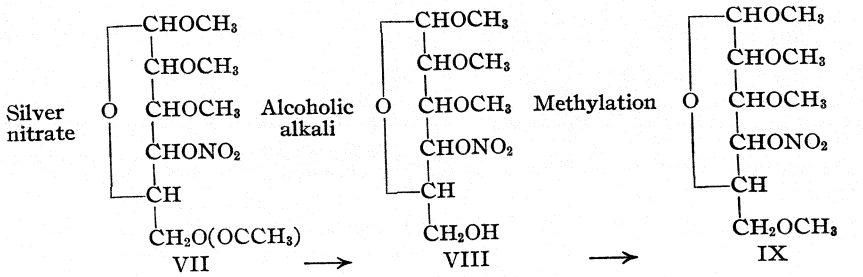



The constitution of compound IV is known as the parent sugar can be oxidized to di-methoxysuccinic acid $\begin{matrix}CHOCH_3—COOH\\ |\\ CHOCH_3—COOH\end{matrix}$ which was identified by conversion into the corresponding dimethoxysuccinamide.[5] There was every assurance, therefore, that the subsequent synthetical reactions were carried out on a substituted methylglucoside containing methyl groups in positions 2 and 3. Advantage was then taken of the reaction discovered by Oldham,[6] who showed that when position 6 of the glucose molecule is nitrated the nitrate group can be replaced by iodine. Dimethylmethylglucoside (IV) was accordingly converted into *2,3-dimethylmethylglucoside-4,6-dinitrate* (V) and thereafter into *2,3-dimethyl-6-iodomethylglucoside-4-nitrate* (VI)

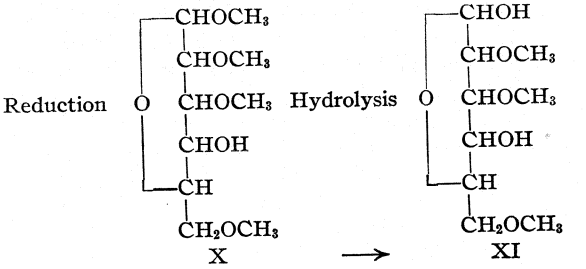



By acting on the iodo derivative with silver acetate and hydrolyzing the product (VII) with alcoholic alkali, 2,3-dimethylmethylglucoside-4-mononitrate (VIII) was obtained and the free hydroxyl group generated in position 6 was thereafter methylated to give 2,3,6-trimethylmethylglucoside-4-mononitrate (IX).

[4] Irvine and Scott, *J. Chem. Soc.*, **103**, 575 (1913).
[5] Purdie and Irvine, *ibid.*, **79**, 957 (1901).
[6] Oldham, *ibid.*, **127**, 2840 (1925).




Finally, the nitrate group was eliminated from position 4 by reduction and the trimethylmethylglucoside (X) thus produced was hydrolyzed to give 2,3,6-trimethylglucose (XI).




The product crystallized readily on nucleation and proved to be identical in every respect with the trimethylglucose obtained from methylated lactose, cellobiose, cellulose, starch and glycogen, On the whole, the synthesis proceeded smoothly although the intermediate compounds were uncrystallizable sirups which could not be further purified by distillation owing to the instability of the nitrate groups. Poor yields were obtained in replacing iodine by acetyl and a complication was introduced by the formation of some trimethylanhydroglucose during the reduction of the nitrate group in position 4. This tendency for nitrogen to be eliminated along with a methyl group is, of course, already well recognized.

## Experimental

The account of the experimental methods is confined to compounds prepared for the first time in the course of the synthesis.

**Nitration of 2,3-Dimethylmethylglucoside.**—Two optional methods were employed, that of Gibson[7] and the simpler process described by Oldham;[6] the latter gives better yields and a purer product. A 5% solution of dimethylmethylglucoside (12 g.) in chloroform containing 30% of nitric acid was kept at room temperature for five minutes and poured into a separating funnel containing ice. After shaking, the chloroform layer was run off and dried over sodium sulfate, the solvent being then removed at 60°. The residue was dissolved in methyl alcohol so as to make a 10% solution and boiled under a reflux condenser for three hours with barium carbonate. On removing

[7] Gibson, *Proc. Roy. Soc. Edinburgh*, **28**, 705 (1908).

the solvent and extracting with ether the product was finally isolated as a sirup which was dried at 100° in a vacuum; yield (13.8 g.) or 89%.

*Anal.* Calcd. for $C_9H_{16}O_{10}N_2$: $OCH_3$, 29.8. Found: $OCH_3$, 30.0.

**Treatment with Sodium Iodide.**—As this reaction is liable to be accompanied by the development of excessive pressures, it is advisable to use only small quantities of the above dimethylmethylglucoside dinitrate in each operation. The dinitrate, in lots of 2.5 g., was dissolved in acetone (10 cc.) and 5 g. of sodium iodide was added, the mixture being thereafter heated in a sealed tube at 100° for six hours. Care has to be exercised in opening the tubes. The product was washed into a flask with acetone, the solvent evaporated and the residue shaken with a mixture of benzene and water. Free iodine was removed by washing the benzene layer with sodium thiosulfate and, after drying, the solvent was evaporated. Only a small proportion of the product was retained by the aqueous layer and this was recovered by extraction with chloroform. The average yield was 2.1 g. in each operation. The product was a sirup which on the evidence of methoxyl and iodine determinations contained some mono-nitrate but the mixture was employed directly in the succeeding reaction.

**Replacement of Iodine by Methoxyl.**—Three series of consecutive reactions were involved. (a) A 10% solution of the above sirup was prepared in acetonitrile and three times the theoretical amount of silver acetate added together with sufficient pyridine to obtain complete solution. On boiling for four hours the whole of the iodine was precipitated as silver iodide and much colloidal silver was formed, the liquid being afterward filtered and evaporated under reduced pressure at 60°. On extracting the residue with ether, the acetate of 2,3-dimethylmethylglucoside mono-nitrate passed into solution and was isolated as usual.

(b) The sirup was dissolved in absolute alcohol so as to form a 5% solution and the theoretical amount of 2 *N* sodium hydroxide added. After thirty minutes the liquid was filtered to remove silver oxide, diluted largely with water and the solution extracted repeatedly with chloroform. Removal of the solvent gave 6.2 g. of a sirup ($n_D$ 1.464) giving analytical figures showing that it consisted essentially of dimethylmethylglucoside mono-nitrate.

(c) Three methylations by means of the silver oxide reaction converted the above sirup into trimethylmethylglucoside mono-nitrate; yield, 6 g.; $n_D$ 1.4595.

*Anal.* Calcd. for $C_{10}H_{19}O_8N$: $OCH_3$, 44.1. Found: $OCH_3$, 43.0.

Up to this stage it was impossible to purify the compounds by distillation owing to the presence of the nitrate group.

**Reduction of the Nitrate Group.**—A 10% solution of the above mono-nitrate in glacial acetic acid was warmed on a water-bath with finely divided iron. Nitrous fumes were evolved and as after forty-five minutes a test sample gave no further reaction with diphenylamine; the reduction was then arrested. The mixture was filtered and largely diluted with water, the total liquid and also the solid residues being repeatedly extracted with chloroform, from which the product was isolated as usual. Impurities were removed by taking up in ether and finally the resulting mobile sirup was distilled at 130–140° (0.2 mm.); yield, 3.6 g.; $n_D$ 1.4595; $OCH_3$, 48.1%. The sirup reacted sharply as a glucoside toward Fehling's solution but the low value for the Zeisel estimation indicates that, as is usually the case, the elimination of nitrogen was accompanied to some extent by anhydro-formation.

**Hydrolysis of the Trimethylmethylglucoside.**—This was carried out according to standard methods and gave a sirup which crystallized readily. After draining on a tile the sugar melted at 108–110° and when recrystallized this value remained unaffected at 114° when the synthetic sugar was mixed with an authentic specimen of

2,3,6-trimethylglucose. In every respect the two specimens were identical in composition and properties; yield 1.8 g.

Acknowledgment is made to the Carnegie Trust for a Research Fellowship awarded to one of us.

## Summary

1. The constitution of 2,3-dimethylglucose has been verified and the sugar has been converted by a sequence of synthetical reactions into 2,3,6-trimethylglucose.

2. These reactions are based on the fact that while 2,3-dimethylglucose gives a di-nitrate, only the nitrate group in position 6 is replaceable by iodine. It was therefore possible to restrict the introduction of the third methyl group to position 6 as positions 4 and 5 were masked.

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[Contribution from the Chemical Laboratory of the University of Buffalo]

# THE REDUCING ACTION OF THE GRIGNARD REAGENT AND THE SYNTHESIS OF TERTIARY ALIPHATIC CARBINOLS

By A. H. Blatt and Julius F. Stone, Jr.

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It was recently shown[1] that a few aliphatic aldehydes and a number of aliphatic ketones were more or less completely reduced to the corresponding primary and secondary alcohols by treatment with certain Grignard reagents. These reductions were roughly correlated with the size and complexity of the alkyl groups present in the carbonyl compound and the reagent and the limits of usefulness of the Grignard reagent in synthesizing aliphatic carbinols were pointed out.

The present work was undertaken in order to secure additional information about the effect of branched chain alkyl groups on the reaction between aliphatic ketones and the Grignard reagent. By the use of a properly chosen series of isomeric ketones and reagents we hoped to learn not only the exact effect of branching the alkyl groups but also, using substances of equal complexity, to learn the effect of the location of the branched groups. We have, therefore, treated each of the three ketones, di-propyl ketone, propyl isopropyl ketone and di-isopropyl ketone, with propyl- and isopropylmagnesium bromides. Some of these reactions had been done before but we found it necessary to repeat certain of them because the reported results were either contradictory or incomplete. We followed in our Grignard reactions what we prefer to term the normal procedure: the addition of the carbonyl compound to an excess of reagent free from excess magnesium. Using this procedure completeness of reaction is as-

[1] Conant and Blatt, This Journal, **51**, 1227 (1929).

sured and any reduction observed can be ascribed definitely to the reagent. The results of our experiments are shown in the table.

TABLE I

RESULTS OF EXPERIMENTS

| | Ketone | Reagent | Addition | Reduction | Enolization | Total |
|---|---|---|---|---|---|---|
| A | $CH_3CH_2CH_2COCH_2CH_2CH_3$ | $CH_3CH_2CH_2MgBr$ | 54[2] | 24 | .. | 78 |
| B | $CH_3CH_2CH_2COCH_2CH_2CH_3$ | $(CH_3)_2CHMgBr$ | 44[2,3] | 5 | 15 | 64 |
| C | $CH_3CH_2CH_2COCH(CH_3)_2$ | $CH_3CH_2CH_2MgBr$ | 63 | 17 | .. | 80 |
| D | $CH_3CH_2CH_2COCH(CH_3)_2$ | $(CH_3)_2CHMgBr$ | 17 | 49[4] | .. | 66 |
| E | $(CH_3)_2CHCOCH(CH_3)_2$ | $CH_3CH_2CH_2MgBr$ | 43[2] | 34 | .. | 77 |
| F | $(CH_3)_2CHCOCH(CH_3)_2$ | $(CH_3)_2CHMgBr$ | 0[1] | 80 | .. | 80 |

The first and second columns of the table give the ketones and reagents used. The next two columns represent the percentages of the original ketone which appeared as addition and reduction product, respectively. The fifth column shows the percentage of the original ketone which was recovered. In view of the work of Grignard[5] and Kohler[6] this material was doubtless present in the reaction mixture as the enolic magnesium derivative. The last column shows the percentage of the original ketone accounted for.

The effect on the reaction between the Grignard reagent and ketones, of branching the alkyl groups present is clearly revealed by the foregoing table. Reactions A, C and E show the effect of branching the alkyl groups (increasing their complexity) in the ketones. This same effect is shown by reactions B, D and F while the comparisons of reactions B with A, D with C, and F with E show the effect of branching the group in the reagent. From these comparisons it can be seen at the outset that it is far more safe to speak of the effect of branched groups in decreasing addition than in increasing reduction. While it is, of course, generally true that reduction increases as the number of branched groups increases the exceptions are so numerous as to emphasize strongly the view previously put forward[7] that reduction is only one of several reactions which come into prominence as addition falls off. The factors deciding which one of these several reac-

[2] These reactions were also done by Stas, (a) *Bull. soc. chim. Belg.*, **34**, 188 (1925); (b) *ibid.*, **35**, 379 (1926), who reported for A, first 37% addition and 10% reduction and later 60% addition and 20% reduction. For B, Stas reported addition only, giving no yield. For E, he reported 30% addition and 30% reduction.

[3] In this reaction we obtained a considerable amount of high-boiling material, apparently condensation products, which we have not included in the above figures.

[4] A sharp separation of reduction and enolization products could not be effected in this experiment.

[5] Grignard and Savard, *Compt. rend.*, **179**, 1573 (1924); *Bull. soc. chim. Belg.*, **36**, 97 (1927).

[6] Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

[7] Ref. 1, p. 1231.

tions (reduction, enolization, condensation) will predominate in a given case are far too complex to allow predictions to be made on the basis of the experimental evidence so far available.

More interesting because more novel and clear-cut is the effect on the reaction of the relative position of the branched groups, *i. e.*, whether present in the ketone or in the reagent. It will be observed that reaction C and reaction B lead to the same addition product. Similarly, the addition product from reaction E is identical with that from reaction D. In C and E straight chain reagents are used, in B and D branched chain reagents. With the straight chain reagents high yields of addition product and clean reactions result; with the branched reagents the yields of addition product are low and the reactions are complicated by numerous side processes. The practical significance of this observation is at once apparent: in the synthesis of tertiary aliphatic carbinols containing branched and straight chain alkyl groups and where the branches are in the $\alpha$-position to the carbinol carbon atom, one should treat a branched chain ketone with a Grignard reagent prepared from a primary straight chain alkyl halide.

The observations most closely related to our own work which we have been able to find are some experiments of Rheinboldt and Roleff,[8] who showed that when certain phenyl alkyl ketones were treated with phenylmagnesium bromide, the result was addition but that when benzophenone was treated with the corresponding alkylmagnesium halide considerable reduction took place. Since phenylmagnesium bromide is not capable of giving the same type of reduction as alkylmagnesium halides, these experiments are not directly comparable with ours. However, it would follow from the work of Rheinboldt and Roleff and that of Blicke and Powers[9] that the preparation of diphenyl alkyl carbinols of any complexity should be carried out by the addition of phenylmagnesium bromide to the phenyl alkyl ketone rather than by the addition of an alkylmagnesium halide to benzophenone.

The expenses of this research have been met with funds privately contributed.

## Experimental

Since the same procedure was employed in all our experiments we shall, in order to save space, describe the procedure at this point and give under the individual reactions only the necessary factual details. Each Grignard reagent employed was prepared in the usual fashion from 1.2 moles each of magnesium and alkyl halide and 500 cc. of ether. After standing overnight the reagent was decanted, through a glass-wool filter, from the excess magnesium, then chilled in an ice- and salt-bath while to it was added

[8] Rheinboldt and Roleff, *Ber.*, **57**, 1921 (1924); *J. prakt. Chem.*, [2] **109**, 175 (1925).

[9] Blicke and Powers, THIS JOURNAL, **51**, 3378 (1929).

0.5 mole of ketone in 100 cc. of ether. The reagent was stirred mechanically during this addition, which required about one hour. No evolution of gas occurred at this stage nor was there any color developed or precipitate formed. The ice-bath was then removed and after stirring for fifteen minutes the reaction mixture was boiled for thirty minutes or until the evolution of gas had ceased. Decomposition of the reaction mixture was then effected by pouring it onto ice to which had been added a slight excess over the theoretical amount of concd. sulfuric acid. The ether and water layers which were then separated were colorless. The water layer was shaken out twice with ether and these extracts were added to the original ether layer. The combined ether extracts were washed with water, sodium carbonate solution and water, then dried over sodium sulfate. Next the ether was removed on the steam-bath and the residual liquid subjected to a series of fractionations at atmospheric or reduced pressure according to the properties of the products.

Propylene was evolved during the reactions as was shown by absorbing it in bromine water and identifying the resulting propylene dibromide by its boiling point, 134–140°.

The ketones employed were prepared by the usual procedure, treatment of an aldehyde with a Grignard reagent followed by oxidation of the secondary alcohol so produced. All the ketones used as well as their reduction products, the secondary alcohols, and their addition products, the tertiary alcohols, have been prepared and described before. Consequently our identification of the reaction products was made by means of their boiling points.

It will be noted that in each of the reactions with the exceptions of B and D, approximately 78% of the starting material was accounted for. The losses of material were due in part, of course, to the difficulty of making a complete separation of the ether and water layers when the reaction mixtures were decomposed. They were due, also, however, to the fact that intermediate fractions in the purification of the reaction products were not counted in estimating the percentage yields. The larger losses in reactions B and D were due to the many transfers occasioned by the fact that the separation of the reaction products required numerous fractionations. No high order of accuracy is claimed for the experiments. In a typical case, however, repetition of an experiment gave essentially identical results.

In the individual experiments next to be described only the significant fractions are given. The forerunnings, intermediate fractions and residues have been omitted.

**A. Di-propyl Ketone and Propylmagnesium Bromide.**—From 57 g. of ketone there was obtained 14 g. of di-propylcarbinol boiling at 150–156° and 43 g. of tri-propylcarbinol[10] boiling at 190–193°.

**B. Di-propyl Ketone and Isopropylmagnesium Bromide.**—From 57 g. of starting material there was recovered 8.9 g. of di-propyl ketone, boiling at 142–144°. In addition we obtained 2.7 g. of di-propylcarbinol, boiling at 153–155°, and 35.1 g. of di-propyl-isopropylcarbinol[2b] boiling at 110° (50 mm.). There was also obtained 6.6 g. of material which boiled at about 130° at 10 mm., apparently a condensation product.

**C. Propyl Isopropyl Ketone and Propylmagnesium Bromide.**—From 57 g. of ketone we obtained 10 g. of propylisopropylcarbinol, 140–146°, and 50.1 g. of di-propyl-isopropylcarbinol, 110° (50 mm.).[2b]

**D. Propyl Isopropyl Ketone and Isopropylmagnesium Bromide.**—In this reaction we were unable to effect a separation of the enolization and reduction products. From 57 g. of ketone we obtained 28.4 g. of material which boiled from 137–147° and was apparently a mixture of ketone and secondary alcohol. The addition product, propyldi-isopropylcarbinol[2b] amounted to 14 g. and boiled at 100° at 50 mm. There was also a small amount, 3.5 g., of high-boiling condensation products. Similar results were ob-

[10] Beilstein–Prager–Jacobson, Julius Springer, Berlin, 1920, Vol. I, p. 426.

tained in a check experiment where it appeared that the low-boiling material was chiefly reduction product.

**E. Di-isopropyl Ketone and Propylmagnesium Bromide.**—From 57 g. of ketone we obtained 19.6 g. of di-isopropyl carbinol boiling at 134–138° and 34.3 g. of propyl di-isopropyl carbinol[2b] boiling at 100° (50 mm.).

## Summary

From a study of the reaction between certain aliphatic ketones and some alkylmagnesium halides it is pointed out that there is no definite and exact correlation between an increase in the complexity of the alkyl groups present and the amount of reduction observed. Further it is shown that the synthesis of tertiary aliphatic carbinols containing both straight and branched chain alkyl groups and where the branches are in the $\alpha$-position to the carbinol carbon atom, should be carried out by the interaction of branched chain ketones and primary straight chain Grignard reagents.

BUFFALO, N. Y.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 77]

# THE DETERMINATION OF THE IONIZATION CONSTANTS OF GUANIDINE AND SOME OF ITS ALKYLATED DERIVATIVES[1]

BY TENNEY L. DAVIS AND ROBERT C. ELDERFIELD[2]

RECEIVED OCTOBER 26, 1931 PUBLISHED APRIL 6, 1932

Guanidine seemingly occupies a unique position among organic bases, for, with the possible exception of the quaternary ammonium and the substituted iodonium bases, it alone approximates the strong fixed alkalies in basic strength. Notwithstanding, the study of its ionization appears to have been largely neglected, while the extent to which the presence of substituents influences its dissociation has attracted no attention whatsoever. In the course of other work which will be reported shortly, information regarding this point was desired, and the results of such an investigation are here presented.

Ostwald[3] made careful measurements of the conductivity of aqueous solutions of guanidine, but there appears to have been no calculation of an ionization constant from these data. Such a calculation shows that guanidonium hydroxide apparently behaves as a strong base. Bredig[4]

[1] The material from which this paper is constructed forms part of a thesis submitted by Robert C. Elderfield to the Faculty of the Massachusetts Institute of Technology in partial fulfilment of the requirements for the degree of Doctor of Philosophy in June, 1930. The results here presented were given as part of a paper on the aliphatic guanidines and nitroguanidines by Tenney L. Davis before the Organic Division of the American Chemical Society at the Atlanta meeting in April, 1930.

[2] The Rockefeller Institute for Medical Research, New York City.

[3] Ostwald, *J. prakt. Chem.*, [2] **33**, 352 (1886).

[4] Bredig, *Z. physik. Chem.*, **13**, 208 (1894).

determined the conductivity of guanidine hydrochloride solutions of various concentrations, and, from calculations based on his data, guanidine again is a strong electrolyte. However, Morell and Bellars[5] determined the ratio of the strength of guanidonium hydroxide to that of sodium hydroxide by three methods, *viz.:* by observing the rate of change of the angle of rotation of a hyoscyamine solution in the presence of the two bases, the ratio was found to be 0.78 : 1; by relative rates of saponification of ethyl acetate, 0.85 : 1, and for barium hydroxide, 0.926 : 1; and by depression of the freezing point of water, 0.81 : 1. Veley[6] measured the hydrolysis of guanidine hydrochloride colorimetrically with methyl orange, and obtained a value for $K_B = 1.1 \times 10^{-8}$ at 15°. This, however, is apparently in error. Matignon[7] determined the heat of neutralization of guanidine to be 14.12 Kg. cal. per gram mole, slightly divergent from the constant value for strong bases.

The present experiments dealt with guanidine and eleven substituted guanidines possessing varying types of substitution as well as of substituents. It appears that guanidine itself is a base of the order of strength of potassium hydroxide. Titration curves of the two are identical within the limits of accuracy of this work. With the exception of the symmetrical di-alkyl derivatives, introduction of aliphatic substituents is without effect on the basicity of the parent compound. Thus, in mono-alkyl, unsymmetrical di-alkyl, and symmetrical tri-alkylguanidines, the character and position of the substituents appears to exert a negligible influence on the ionization. In phenylguanidine, the only aromatic one studied, as would be expected the introduction of the phenyl group diminishes the basic properties. In the case of the symmetrical di-alkylguanidines, a curious anomaly appears. These substances are markedly weaker in basic properties than the others, but here again, the character of the substituents seems to exert a negligible influence. Hence the statement may be made that in the cases studied the ionization of the alkylated guanidines is determined solely by the position of the substituents, and is independent of the character of the latter.

## Description of Experiments

For the determination of the basic strength of the compounds under consideration, the method chosen was that embracing the use of titration curves. The apparatus used consisted of a 250-cc. wide-mouthed Erlenmeyer flask fitted with a three-holed stopper slotted at one place on the periphery. Through the holes were passed a glass tube for the hydrogen half-cell, the buret tip, and a saturated potassium chloride bridge. The latter led to another 250-cc. wide-mouthed Erlenmeyer serving as a potassium chloride reservoir which in turn was joined to a saturated calomel half-cell by means of a

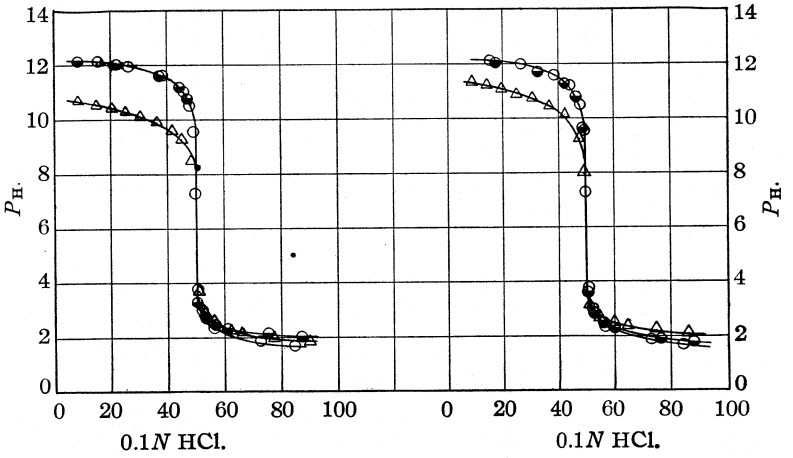
[5] Morell and Bellars, *J. Chem. Soc.*, **91**, 1012 (1907).

[6] Veley, *ibid.*, **93**, 660 (1908).

[7] Matignon, *Ann. chim. phys.*, [6] **28**, 88 (1893).

second saturated potassium chloride bridge. The hydrogen half-cell was of the Hildebrand type. The whole apparatus was immersed in a thermostat held at 25 ± 2°. The potentiometer system was of the standard type using a student type potentiometer and a portable galvanometer. The accuracy of the measurements is about 0.05 $P_H$ units. The saturated calomel half-cell was checked from time to time against a 0.05 molal potassium acid phthalate solution.

In order to prepare a solution of any guanidine, the sulfate was used as starting material. These are well crystallizable salts easily obtainable in a high degree of purity. An exactly 0.05 normal solution of the sulfate under examination was prepared and 100 cc. of this solution was placed in the titration vessel. A stream of hydrogen was then passed through to sweep out any carbon dioxide. To the solution was added 0.1 normal barium hydroxide in quantity exactly sufficient to precipitate all the sulfate and thus give a solution of the free base. The latter was then titrated with 0.1 normal hydrochloric acid without filtering off the precipitated barium sulfate. For reference purposes an exactly similar titration was made using potassium sulfate.




◒, 150 cc. of 0.033 molar guanidine titrated with 0.1 *N* HCl;
○, similar data for KOH;
△, similar data for N,N′-dimethylguanidine.

◒, 150 cc. of 0.033 molar piperidoguanidine titrated with 0.1 *N* HCl;
○, similar data for KOH;
△, similar data for phenylguanidine.

Fig. 1.

The results thus obtained are summarized in Table I. In the cases of the highly ionized strong bases no attempt was made to calculate an ionization constant, as the evidence clearly justified the assumption of complete ionization. The curves were merely plotted on the same graph with that of potassium hydroxide, typical examples of which are shown in Fig. 1. The others coincided equally as well within the limits of experimental error. In the case of the weaker bases, the constants were determined by the usual method from the titration curves. Typical curves for these substances are also shown in Fig. 1.

TABLE I

RESULTS OF EXPERIMENTS

| Guanidine | $K \times 10^{-4}$ | Sulfate M. p., °C. | Sulfate Recryst. from | Sulfate Analysis, % $SO_4$ Calcd. | Sulfate Analysis, % $SO_4$ Found | Nitrate M. p., °C. | Nitrate Recryst. from | Nitrate Analysis, % N Calcd. | Nitrate Analysis, % N Found | Picrate M. p., °C. | Picrate Recryst. from | Picrate Analysis, % N Calcd. | Picrate Analysis, % N Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Guanidine[a] | Large | 300 dec. | Alc.-Aq. | | | 212 | Aq. | | | 310 dec. | Alc. | | |
| Methyl- | Large | 238–9 dec. | MeOH-Aq. | | | 150 | Aq. | | | 200 | Alc.-Aq. | | |
| *n*-Butyl- | Large | 206 | MeOH-BuOH | 29.28 | 29.34 | 69 | Alc. | 31.46 | 31.22 | 154.5 | Alc.-Aq. | 24.42 | 24.46 |
| *n*-Heptyl- | Large | 244 dec. | Alc.-Ether | 23.32 | 23.21 | 86 | Aq. | 25.61 | 25.41 | 140.5 | Alc.-Aq. | 22.79 | 22.62 |
| Benzyl-[b] | Large | 204 | MeOH | 24.25 | 24.15 | 165 | Aq. | 26.40 | 26.46 | 185.5 | Alc. | 21.21 | 21.77 |
| Piperido- | Large | Above 270 | Aq. | | | 154 dec. | Aq. | 29.63 | 29.45 | 244.5 | Alc. | | |
| NN-Dimethyl- | Large | 285–7 dec. | Alc.-Aq. | | | 141 | Aq. | | | 224 | Alc.-Aq. | | |
| NN′-Dimethyl- | 1.95 | 264–5 dec. | Alc.-Aq. | 35.51 | 35.48 | 68 | Aq. | 37.32 | 37.49 | 178 | Alc.-Aq. | | |
| NN′-Diethyl- | 2.00 | 234–5 dec. | Alc.-Ether | 29.28 | 29.43 | | | | | 141 | Alc.-Aq. | | |
| NN′-Di-*n*-amyl- | 1.78 | 190–1 dec. | Alc.-Ether | 19.35 | 19.26 | | | | | 108 | Benzene | 19.63 | 19.71 |
| NN′N″-Trimethyl- | Large | Above 345 | Alc.-Ether | 32.01 | 32.19 | 276 | Alc. | 34.15 | 34.46 | 214.5 | Alc.-Aq. | 25.46 | 25.85 |
| Phenyl- | 5.89 | 205 | Water | | | | | | | 222 | Alc. | | |

[a] After this work had been completed an article by Hall [THIS JOURNAL, **52,** 5125 (1930)] appeared wherein the $pK_H$ value for guanidine as determined by titration in acetic acid is given as 13.5, thus confirming the conclusions here reached.

[b] Benzyl guanidine bicarbonate is very characteristic, being extremely insoluble in cold water and more readily in hot from which it is deposited in long thick needles. *Anal.* $CO_2$ (Geissler alkalimeter). Calcd.: 20.95. Found: $CO_2$, 20.62.

**Preparation of Materials.**—The guanidine salts were prepared from guanidine carbonate which was in turn prepared from nitroguanidine and ammonium carbonate.[8] The mono-alkyl and NN-dialkylguanidines were prepared according to Clarke and Phillips[9] the sulfates thus obtained being metathesized into the nitrates by means of barium nitrate. The NN′-dialkylguanidines were prepared according to Kaess and Gruszkiewicz.[10] NN′N″-Trimethylguanidine was prepared according to Hoffmann[11] Phenylguanidine was prepared by the method of Smith[12] The melting points of the various derivatives together with analyses of those previously undescribed in the literature are shown in Table I.

***n*-Heptylamine.**—This was prepared by the interaction of *n*-heptyl bromide and ammonia, which preparation does not seem to have been described in the literature; 92 g. of *n*-heptyl bromide (b. p. 176–178°) was dissolved in 800 cc. of methyl alcohol, and the mixture saturated with ammonia and allowed to stand at room temperature one week. After breaking up the amine hydrobromides with sodium hydroxide, the amines were fractionated in a current of nitrogen. The yields were: *n*-heptylamine, b. p. 155–158°, 28 g.; di-*n*-heptylamine, b. p. 270–275°, 20 g.; tri-*n*-heptylamine, trace.

## Summary

1. The ionization of twelve alkylated guanidines of varying types of substitution has been studied.

2. Basic strength in this series of compounds, wherever aliphatic substituents occur, appears to be a function only of the positions of the substituents. A phenyl group diminishes the basicity.

3. Twenty new substituted guanidine salts are described.

4. General details for the synthesis of amines have been given in the preparation of *n*-heptylamine.

CAMBRIDGE, MASSACHUSETTS

[8] Davis and Abrams, *Proc. Am. Acad.*, **61**, 437 (1926).

[9] Clarke and Phillips, THIS JOURNAL, **45**, 1755 (1923).

[10] Kaess and Gruszkiewicz, *Ber.*, **35**, 3598 (1902).

[11] Hoffmann, *ibid.*, **2**, 600 (1869); Schenck, *Arch. Pharm.*, **247**, 466 (1909).

[12] Smith, THIS JOURNAL, **51**, 476 (1929).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

# SOME MONO AND DIBROMO DERIVATIVES OF META-CRESOL

BY RALPH C. HUSTON AND JAMES A. HUTCHINSON

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The literature gives very little information concerning the bromine derivatives of *m*-cresol. Descriptions of the mono and dibromo derivatives are meager and often contradictory. In some cases definite proof of structure is entirely lacking. Because a more definite knowledge of these seemed desirable and because a knowledge of the structure of some of them was essential in determining the configuration of certain benzylated derivatives of *m*-cresol, the present study was undertaken.

## Monobromo-*m*-Cresols[1]

**Direct Bromination.**—One hundred and eight grams of purified *m*-cresol was dissolved in 200 cc. of chloroform, cooled to −10°, and stirred continuously while 160 g. of bromine in 100 cc. of chloroform was added at such a rate that the temperature did not at any time exceed −5°. After all of the bromine had been added the stirring was continued for thirty minutes and the mixture was allowed to stand overnight. After several distillations, 26 g. came over at 120–130°, and 155 g. at 130–140° (16 mm.).

When repeatedly distilled at atmospheric pressure (731 mm.), the 120–130° fraction came over at 205–208°. A sample dissolved in chloroform and treated with one molecular equivalent of bromine gave an excellent yield of 4,6-dibromo-3-methylphenol, which melted at 65–66° and gave a benzoyl derivative melting at 84–85° (see below).

*Anal.* Calcd. for $C_7H_7OBr$: Br, 42.78. Found: Br, 42.29.

The 130–140° fraction solidified and was repeatedly crystallized from petroleum ether. It came down in long colorless silky needles which tended to mat together and melted at 56–57°. In some cases it was crystallized from water.

*Anal.* Calcd. for $C_7H_7OBr$: Br, 42.78. Found: Br, 42.59, 42.65.

**Preparation of 6-Bromo-3-methylphenol from 4-Bromo-3-aminotoluene.**—Acet-*p*-toluidide was nitrated[2] and the acyl group removed by means of alcoholic potash. The amino group was replaced by bromine through the diazonium perbromide[3] and the nitro group reduced by means of tin and hydrochloric acid to form 6-bromo-*m*-toluidine[4] melting at 32–33° and boiling at 115–118° (16 mm.).

The 6-bromo-*m*-toluidine was dissolved by boiling with dilute hydrochloric acid. When cooled the hydrochloride separated out. The mixture was cooled to 0°, and the calculated amount of sodium nitrite in water solution was added with constant stirring. After two hours the diazonium salt was decomposed by heating on the water-bath. Steam distillation gave a reddish-yellow oil. This was salted out and extracted with ether. After removal of the solvent the residue was treated with dilute sodium hydroxide and filtered. The filtrate was acidified with dilute hydrochloric acid, salted out and

[1] Neville and Winther, *Ber.*, **15**, 2991 (1882); Walther and Zipper, *J. prakt. Chem.*, [2] **91**, 376 (1915); Hodgson and Moore, *J. Chem. Soc.*, 2038 (1926); Hodgson and Beard, *ibid.*, 498 (1926); Darzens and Levy, *Compt. rend.*, **193**, 292 (1931).

[2] Gattermann, *Ber.*, **18**, 1483 (1885).

[3] Bulow and Schmactenberg, *ibid.*, **41**, 2609 (1908).

[4] Neville and Winther, *ibid.*, **13**, 972 (1880); *cf.* Wroblewsky, *Ann.*, **168**, 177 (1873).

extracted with ether. The 6-bromo-3-methylphenol obtained by distillation of the ether extract was proved by boiling point (206–208° at 731 mm.), analysis, and bromination to 4,6-dibromo-3-methylphenol to be identical with the liquid monobromo-*m*-cresol obtained by direct bromination.

**Preparation of 4-Bromo-3-methylphenol from 2-Bromo-5-aminotoluene.**—Acet-*m*-toluidine was brominated in acetic acid. The acyl group was removed and the 4-bromo-*m*-toluidine crystallized from alcohol to a constant melting point of 79–80°.[5] The purified amine was dissolved in much dilute hydrochloric acid, cooled to 0° and diazotized with the calculated amount of sodium nitrite. After two hours the diazonium salt was decomposed by heating on the water-bath, and steam distilled. The resulting yellow oil was salted out and extracted with ether. After purification of the crude phenol by dissolving in alkali, filtering and reprecipitating with acid, it was extracted with ether, and recrystallized from petroleum ether. It was identical in crystal form and melting point with the solid monobromo-*m*-cresol obtained by direct bromination. The yield was approximately 25%.

*Anal.* Calcd. for $C_7H_7OBr$: Br, 42.78. Found: Br, 42.72.

**Esters of 4-Bromo-3-methylphenol.**—Benzoic, benzenesulfonic and *p*-toluenesulfonic esters were prepared from 4-bromo-3-methylphenol obtained both by direct bromination and by diazotization of 4-bromo-*m*-toluidine. The pyridine method was used.[6]

| | Crystal form (from alcohol) | M. p., °C. | Bromine, % Calcd. | Found |
|---|---|---|---|---|
| Benzoic ester | Fine white fluffy needles | 82.5–83 | 27.32 | 27.5 |
| Benzenesulfonic ester | Long white needles | 79–80 | 24.46 | 24.19 |
| *p*-Toluenesulfonic ester | Small lustrous plates | 84–85 | 23.46 | 23.25 |

### Dibromo-*m*-Cresols[7]

**Direct Bromination.**—One hundred and eight grams of *m*-cresol was brominated with 320 g. of bromine under the same experimental conditions as were used in the preparation of the monobromo-*m*-cresols. Upon distillation practically all of the product came over at 130–140° (16 mm.) and solidified. Recrystallization from petroleum ether gave flat needles melting at 64–65°. Evaporation of the mother liquor gave an oil which did not solidify at room temperature, and distilled at 132–135° (16 mm.). The crystalline compound was shown by analysis to be a dibromo-*m*-cresol.

*Anal.* Calcd. for $C_7H_6OBr_2$: Br, 60.15. Found: Br, 59.93.

Its sodium salt reacted with benzyl chloride in toluene to give an *ortho* benzyl derivative.[8] The benzoyl derivative, prepared by the pyridine method, crystallized from alcohol in mats of very fine needles melting at 80–81°.

*Anal.* Calcd. for $C_{14}H_{10}O_2Br_2$: Br, 43.2. Found: Br, 42.35.

Since this phenol has an unsubstituted ortho position, it must be either 2,4-dibromo-3-methylphenol or 4,6-dibromo-3-methylphenol.

The oil (b. p. 132–135°) obtained from the filtrates was seeded with a crystal of 4,6-dibromo-3-methylphenol prepared from the amine (see below). It solidified. After chilling it was pressed between pads of filter paper to remove oily impurities, and recrystallized from petroleum ether. Analysis, melting point (65–66°) and melting point of the benzoyl derivative (84–85°) proved it to be 4,6-dibromo-3-methylphenol.

[5] Neville and Winther, *Ber.*, **13**, 963 (1880).

[6] Einhorn and Holland, *Ann.*, **301**, 95 (1898).

[7] Gibbs and Robertson, *J. Chem. Soc.*, **105**, 1891 (1914); *ibid.*, **105**, 1888 (1914).

[8] Huston and Houk, THIS JOURNAL, **54**, 1506 (1932).

*Anal.* Calcd. for $C_7H_6OBr_2$: Br, 60.15. Found: Br, 60.01.

The less soluble phenol formed with it is therefore the 2,4-dibromo-3-methylphenol.

**Preparation of 4,6-Dibromo-3-methylphenol from 3-Amino-4,6-dibromotoluene.**—Pure *m*-toluidine was acylated and treated in cold acetic acid solution with two molecular equivalents of bromine. The acyl group was removed by means of alcoholic potash, and the 4,6-dibromo-*m*-toluidine was recrystallized from alcohol to a constant melting point of 75–76°.[9] The purified amine was dissolved in hot, dilute hydrochloric acid, filtered and cooled to 0°. The calculated quantity of sodium nitrite was slowly added and the mixture was stirred until solution was complete. After two hours the diazonium salt was decomposed by heating on the water-bath and the dark colored mixture was steam distilled. The distillate was salted out and extracted with ether. After evaporation of the solvent the phenol was separated from the quinone by dissolving in dilute sodium hydroxide, reprecipitating with hydrochloric acid, and extracting with ether. The purified 4,6-dibromo-3-methylphenol crystallized from petroleum ether in fine flat crystals which cling to the sides of the beaker. The melting point (65–66°) is ten degrees higher than that given by Gibbs and Robertson.[7] The benzoyl derivative came down from alcohol in fine needles melting at 84–85°.

*Anal.* Calcd. for $C_{14}H_{10}O_2Br_2$: Br, 43.2. Found: Br, 43.78.

## Summary

Bromination of *m*-cresol in the cold with one molecular equivalent of bromine gave a mixture of 4-bromo-3-methylphenol and 6-bromo-3-methylphenol.

Bromination of *m*-cresol with two molecular equivalents of bromine gave a mixture of 2,4-dibromo-3-methylphenol and 4,6-dibromo-3-methylphenol.

[9] Neville and Winther, *Ber.*, **13**, 971 (1880).

EAST LANSING, MICHIGAN

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

# ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. VIII. BENZYLATION OF META-CRESOL

BY RALPH C. HUSTON AND ALVA L. HOUK

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This completes a series of three articles from this Laboratory on the benzylation of the cresols.[1]

*m*-Cresol treated with benzyl alcohol and aluminum chloride in petroleum ether gave two monobenzyl cresols and one dibenzyl cresol: 3-methyl-4-benzylphenol,[2] 3-methyl-6-benzylphenol and 3-methyl-4,6-dibenzylphenol. When treated with sodium and benzyl chloride in toluene (Claisen reaction)[3] it gave also two monobenzyl cresols and one dibenzyl cresol: 3-methyl-2-benzylphenol, 3-methyl-6-benzylphenol and 3-methyl-2,6-dibenzyl-

[1] Huston and others, THIS JOURNAL, **52**, 4484 (1930); **53**, 2379 (1931).

[2] Venturi, *Gazz. chim. ital.*, **31**, I, 472 (1901).

[3] Claisen, *Ann.*, **442**, 221 (1924).

phenol, and a trace of the dibenzyl derivative obtained in the aluminum chloride condensation. This is interesting in that it represents a small amount of para substitution by the Claisen reaction. Both types of condensation yielded 3-methyl-6-benzylphenol as the only common product. In the Claisen condensation a small amount of the ether, 3-methylphenyl benzyl ether, was isolated.

The 3-methyl-2,6-dibenzylphenol was also prepared from 3-methyl-2-benzylphenol and benzyl chloride by the Claisen reaction. This condensation gave a small amount of the ether, 2-benzyl-3-methylphenyl benzyl ether.

Benzoyl derivatives of all the benzylated cresols were prepared, and bromine derivatives of all except 3-methyl-2,6-dibenzylphenol, this bromine derivative being, like the benzylated cresol itself, a liquid and obtained in our work in insufficient quantity to purify.

In order to establish the structures assigned to the various benzylated cresols, two dibromo-*m*-cresols were benzylated by the Claisen method. In 2,4-dibromo-*m*-cresol[4] only the 6-position is available for the benzyl group to enter. The product obtained, 2,4-dibromo-3-methyl-6-benzylphenol, was identical with that obtained by brominating 3-methyl-6-benzylphenol. The 2,4-dibromo-*m*-cresol used was prepared by direct bromination of *m*-cresol and melted at 64–65°.

The benzylation of 4,6-dibromo-*m*-cresol,[4] prepared from 4,6-dibromo-*m*-toluidine by diazotization to the phenol (m. p. 65–66°), gave the other *o*-benzyl derivative, 4,6-dibromo-3-methyl-2-benzylphenol, the same compound that was prepared by brominating 3-methyl-2-benzylphenol.

It is worthy of note that the aluminum chloride method did not introduce a benzyl group between the phenolic hydroxyl and the methyl group of *m*-cresol; also that of the two monobenzyl derivatives in which the benzyl groups are ortho to the phenolic hydroxyl, the one which is the more compact and symmetrical has the higher melting point.[5]

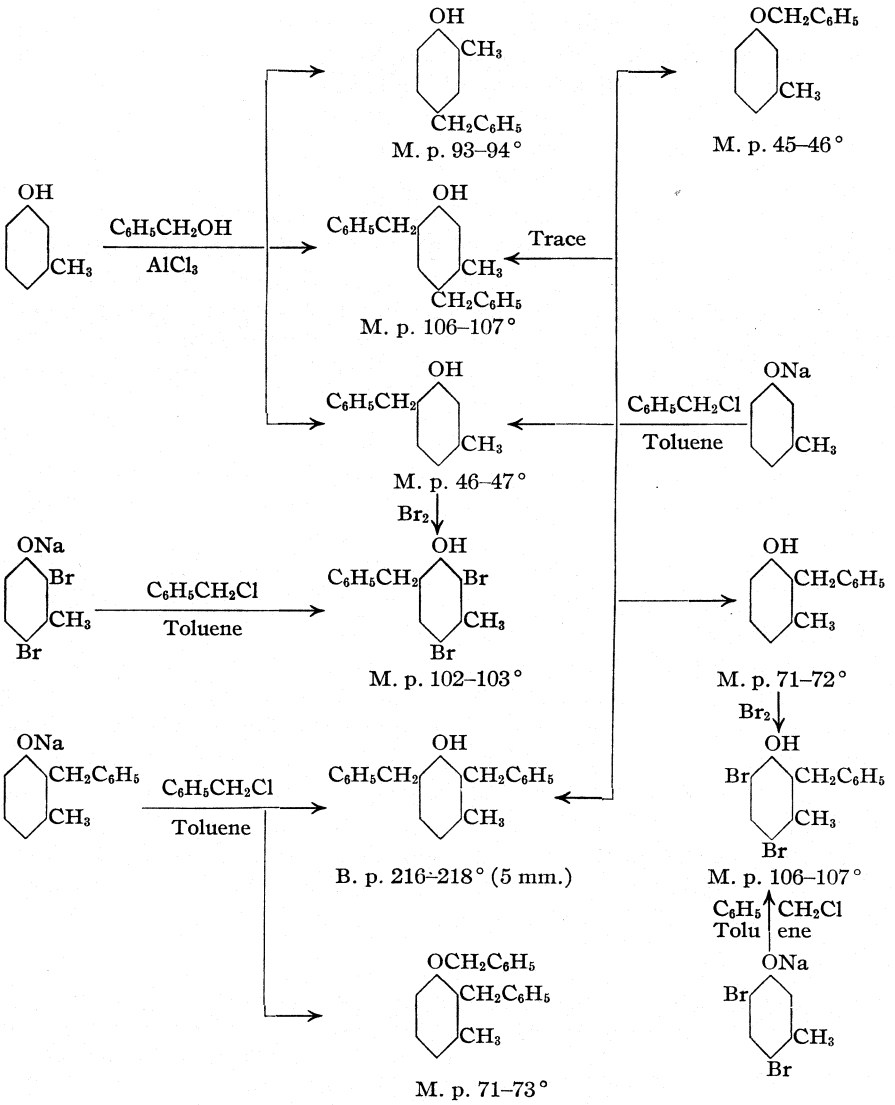
## Experimental

**Benzylation of *m*-Cresol by the Aluminum Chloride Method.**—A mixture of 120 g. of *m*-cresol, 100 g. of benzyl alcohol, and 150 g. of petroleum ether was placed in a tall vessel and stirred constantly during the addition of 60 g. of aluminum chloride over a period of about two hours. The temperature was maintained at about 35° and additional petroleum ether was added occasionally. Hydrogen chloride was given off copiously and the substance became a light brown viscous mixture. After standing overnight it was decomposed with ice, extracted with ether and distilled. The following fractions were obtained at 4 mm.: 125–140°, 6.0 g.; 140–165°, 38.0 g.; 165–185°, 33.0 g.; 185–250°, 46.5 g.

**3-Methyl-6-benzylphenol.**—The fraction 140–165° boiled mostly at 153–157°. It was a thick yellow oil which solidified after standing for some time in the refrigerator. Crystallization had to be carried out in a cold place. The substance came out in a mass

[4] Huston and Hutchinson, THIS JOURNAL, **54**, 1504 (1932).

[5] Carnelley, *Phil. Mag.*, [5] **13**, 116 (1882).




of white, felted, needle-like crystals melting at 46–47° and boiling at 153–155° (4 mm.). This was also prepared by the Claisen method.

*Anal.* Subs., 0.2797, 0.3157: $CO_2$, 0.8638, 0.9719; $H_2O$, 0.1792, 0.2004. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.12. Found: C, 84.23, 83.96; H, 7.17, 7.10.

**3-Methyl-4-benzylphenol.**—The fraction 165–185° solidified in the receiver and was crystallized from petroleum ether in colorless prisms melting at 93–94° and boiling at 168–170° (5 mm.).

*Anal.* Subs., 0.2154: $CO_2$, 0.6680; $H_2O$, 0.1381. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.12. Found: C, 84.57; H, 7.17.

**3-Methyl-4,6-dibenzylphenol.**—The fraction 185–250° nearly all came over at 220–230° and solidified to form an oily mass which, after several crystallizations, came out as a very soft, felted, white mass, melting at 106–107° and boiling at 230–232° (5 mm.).

The assignment of structure was based upon the non-formation of 3-methyl-2-benzylphenol by the aluminum chloride method.

*Anal.* Subs., 0.1902, 0.1908: $CO_2$, 0.6074, 0.6059; $H_2O$, 0.1184, 0.1194. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 7.00. Found: C, 87.09, 86.60; H, 6.96, 7.00.

**Benzylation of *m*-Cresol by the Claisen Method.**—11.4 g. of finely cut sodium was suspended in 125 g. of toluene and 54 g. of *m*-cresol added. The mixture reacted rapidly to form a white cheesy mass, the temperature being controlled by immersing the flask in cold water. After standing overnight 64 g. of benzyl chloride was added and the mixture refluxed on an oil-bath at 150° for five hours. When cooled, it was washed twice with water to remove the sodium chloride and the toluene distilled off. The residue was dissolved in 250 cc. of Claisen's alcoholic potash[6] and extracted with 200 cc. of petroleum ether in 50-cc. portions to remove any ether present. The potash solution was neutralized with 6 *N* hydrochloric acid and extracted with ether. The ether was removed and the residue fractionated: 125–140°, 8.5 g.; 140–160°, 34.5 g.; 160–230°, 12.5 g.

**3-Methylphenyl Benzyl Ether.**—The petroleum ether extract, containing the Claisen's ether, distilled at 280–290°, decomposing above 290°. At 5 mm. it boiled at 142–145° and crystallized into white platelets melting at 45–46°. These points vary somewhat from those given by Staedel[7] but his work was repeated, giving results identical with the above.

**2-Benzyl-3-methylphenol.**—The fraction 140–160° contained two isomers, one solidifying and the other remaining as an oil. These were separated by pressing the mass between filter papers, which absorbed the oily compound and it could then be extracted with ether. The ether extract gave an oil boiling at 153–155° (4 mm.) and solidifying into crystals melting at 46–47°, which proved to be 3-methyl-6-benzylphenol, identical with that prepared by the aluminum chloride condensation.

The crystals from this fraction, after being pressed between filter papers, were crystallized from petroleum ether, giving long, regular needles melting at 71–72° and boiling at 157–159° (5 mm.).

*Anal.* Subs., 0.1769, 0.2256: $CO_2$, 0.5483, 0.6993; $H_2O$, 0.1127, 0.1428. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.12. Found: C, 84.53, 84.53; H, 7.13, 7.08.

**3-Methyl-2,6-dibenzylphenol.**—The fraction 160–230° was a heavy yellow oil which, on standing, yielded a very small amount of crystalline material which proved to be the dibenzyl derivative obtained by the aluminum chloride method, 3-methyl-4,6-dibenzylphenol. The remainder of the oil did not solidify but after several distillations boiled at 216–218° (5 mm.). This compound was also prepared from the monobenzyl derivative, 2-benzyl-3-methylphenol, and benzyl chloride by the Claisen reaction.

*Anal.* Subs., 0.2145: $CO_2$, 0.6869; $H_2O$, 0.1335. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 7.00. Found: C, 87.33; H, 6.96.

**2-Benzyl-3-methylphenyl Benzyl Ether.**—In the formation of 3-methyl-2,6-dibenzylphenol from 3-methyl-2-benzylphenol by the Claisen method, a small amount of the corresponding Claisen ether was isolated. The method of condensation was exactly as described previously. The petroleum ether extract solidified as soon as the petroleum ether had evaporated. Recrystallized from alcohol, the ether formed fine yellowish needles melting at 71–73°.

[6] Claisen, *Ann.*, **442**, 224 (1924).

[7] Staedel, *ibid.*, **217**, 46 (1882).

*Anal.* Subs., 0.0804: $CO_2$, 0.2568; $H_2O$, 0.0505. Calcd. for $C_{21}H_{20}O$: C, 87.45; H, 7.00. Found: C, 87.10; H, 7.03.

**Bromine Derivatives.**—The calculated molecular quantities of bromine were added to the chloroform solutions of the benzylated cresols with vigorous reaction and copious evolution of hydrogen bromide. In most cases the bromine derivative solidified on evaporation of the chloroform. Petroleum ether and alcohol were both used as crystallizing agents but the better results were obtained with alcohol.

The 4,6-dibromo-3-methyl-2-benzylphenol and the 2,4-dibromo-3-methyl-6-benzylphenol were prepared also in good yields by treating the corresponding dibromocresolates[4,5] in toluene with benzyl chloride, refluxing at 150–160°, and extracting as in the benzylation of *m*-cresol, by the Claisen method. The benzylated products came down as solids upon evaporation of the ether extracts.

TABLE I

BROMO DERIVATIVES

| Derivation of benzylphenol | Crystal form and solvent | M. p., °C. | Bromine, % Calcd. | Found |
|---|---|---|---|---|
| 2,6-Dibromo-3-methyl-4- | Shiny tan leaflets from alc. | 86–87 | 44.91 | 44.23, 44.25 |
| 2,4-Dibromo-3-methyl-6- | Fine felted needles from alc. or pet. ether | 102–103 | 44.91 | 44.81 |
| 4,6-Dibromo-3-methyl-2- | White felted needles from alc. | 106–107 | 44.91 | 44.75 |
| 2-Bromo-3-methyl-4,6-di- | White platelets from alc. or pet. ether | 65–67 | 21.76 | 21.38 |

**Benzoyl Derivatives.**—Esterification was accomplished by the Schotten–Baumann reaction.

TABLE II

BENZOATES OF BENZYLPHENOL DERIVATIVES

| Benzoates of benzylphenol | Crystal form and solvent | M p., °C. | Carbon, % Calcd. | Found | Hydrogen, % Calcd. | Found |
|---|---|---|---|---|---|---|
| 3-Methyl-4- | Rosets from pet. ether; thin plates from alc. | 70–71 | 83.40 | 83.03 | 6.00 | 5.99 |
| 3-Methyl-6- | Fine needles from alc. | 58–59 | 83.40 | 83.13 | 6.00 | 6.14 |
| | | B. p. (5 mm.) 215–220° | | | | |
| 3-Methyl-2- | Shiny platelets from alc. | 71–73 | 83.40 | 83.20 | 6.00 | 5.95 |
| 3-Methyl-4,6-di- | Fine fluffy needles from alc. or pet. ether | 88–89 | 85.67 | 85.13 | 6.17 | 5.89 |
| 3-Methyl-2,6-di- | Thick yellow oil | ... | 85.67 | 85.55 | 6.17 | 6.36 |
| | | B. p. (5 mm.) 235–240° | | | | |

## Summary

1. Meta-cresol was benzylated by the aluminum chloride and the Claisen methods, giving three monobenzyl and two dibenzyl derivatives.

2. Bromine and benzoyl derivatives of the benzylated cresols were prepared.

3. Two of the bromine derivatives were also prepared by benzylating known bromocresols, thus establishing the structures of the compounds.

EAST LANSING, MICHIGAN

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

# *PARA*-AMINOPHENYLGUANIDINE: THE PREPARATION OF THE NITRATE, HYDROCHLORIDE AND SULFATE SALTS, AND ATTEMPTED PREPARATION OF THE FREE BASE

BY CHARLES E. BRAUN

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## Introduction

It was considered advisable in the course of a physiological investigation of the hypoglycemic properties of *p*-aminophenylguanidine to prepare salts of this base other than the hydroiodide in order to eliminate the possibility of thyroid complications. Therefore the nitrate, hydrochloride and sulfate salts were prepared, and the hypoglycemic properties of the last two were investigated. Since the results of the physiological work have been reported,[1] this paper will treat only the methods of synthesis of these compounds, and some observations noted during the attempted preparation of the free base.

## Experimental

***p*-Aminophenylguanidine Nitrate.**—To 26 g. (0.0935 mole) of *p*-aminophenylguanidine hydroiodide[2] in 700 cc. of cold water was added 16 g. (0.0940 mole) of silver nitrate in 500 cc. of water. After adding 5 g. of charcoal (*norite*) the mixture was agitated for five days at room temperature and filtered. The filtrate was treated with hydrogen sulfide, concentrated to about 75 cc., boneblacked and refiltered. Upon cooling, the concentrate set to an almost solid mass of crystals. These were washed with cold absolute alcohol and cold absolute ether, and dried at room temperature *in vacuo*. The crude yield (m. p. 183–186°) was 13.0 g. or 65.3%.

The crude salt was purified by three recrystallizations from water under an atmosphere of hydrogen sulfide. The purified nitrate was white, crystalline, and melted at 189–190°. It was stable when dry, but discolored upon standing in aqueous solution. Its solubilities in weight per cent. at 25° were: water, 1.81; absolute methyl alcohol, 1.55. The final yield (purified salt) was 6.0 g. or 30.1%.

*Anal.* Calcd. for $C_7H_{11}N_5O_3$: N, 32.86. Found: N, 32.73 (by modified Kjeldahl), 33.09 (by micro Dumas).

***p*-Aminophenylguanidine Hydrochloride.**—Equivalent quantities (0.32 mole) of *p*-phenylenediamine (Eastman product recrystallized from benzene, m. p. 140.5–141°) and S-ethyl isothiourea hydrochloride (prepared according to Stevens, m. p. 95–97°)[3] in 25 cc. of cold water were heated under reflux on a boiling water-bath for two and one-half hours, during which time air was blown over but not through the reaction mass to facilitate the removal of the ethyl mercaptan evolved during the condensation. The volume of the reaction mass was then reduced by heating under reduced pressure. Upon cooling the concentrate set to a semi-solid mass of crystals, which were disintegrated by grinding under absolute alcohol. This solvent removed almost completely the purple mother liquor, leaving behind, after filtration, a grayish white material,

[1] T. B. Parks and C. E. Braun, *J. Biol. Chem.*, **91**, 629 (1931).

[2] C. E. Braun, *ibid.*, **89**, 97 (1930).

[3] H. P. Stevens, *J. Chem. Soc.*, **81**, 80 (1902).

which, after washing with cold absolute alcohol and absolute ether, was dried at room temperature *in vacuo*. The crude yield (m. p. 165–167°) was 25 g. or 41.9%.

The crude compound was purified by two reprecipitations from alcohol–water solution by the addition of ether, and one recrystallization from absolute alcohol. The purified hydrochloride, not absolutely white but having a slight yellowish tint, was crystalline and melted at 167–168.5°. It was stable when dry but quickly discolored in aqueous or alcoholic solution. Its solubilities in weight per cent. at 25° were: water, 49.11; absolute methyl alcohol, 24.78. The final yield (purified salt) was 9 g. or 15.08%.

*Anal.* Calcd. for $C_7H_{11}N_4Cl$: Cl, 19.00. Found: Cl, 19.02 (as AgCl).

**p-Aminophenylguanidine Sulfate.**—Equal weights (56 g.) of S-methyl isothiourea sulfate (prepared according to Arndt, m. p. 245°)[4] and *p*-phenylenediamine (m. p. 140.5–141°) in 60 cc. of water were heated under reflux on a boiling water-bath for two hours. The reaction mass was then transferred to a beaker and chilled. Upon cooling the entire mass set to a crystalline paste. The latter, after the addition of 50 cc. of alcohol was filtered, washed on the funnel with alcohol and dried at room temperature *in vacuo*. The crude sulfate was almost white and had a decomposition range of 260–276° when heated at a rate of 1° per second. The crude yield was 71 g. or 88.56%.

The crude salt was purified by two reprecipitations from aqueous solution by the addition of alcohol, keeping the solution saturated with hydrogen sulfide to prevent discoloration. The purified sulfate was white, crystalline and decomposed at 279° when heated at the rate of 1° per second. It was stable when dry but discolored very slowly in aqueous solution. Its solubilities in weight per cent. at 25° were: water, 10.23; absolute methyl alcohol, 0.10. The final yield (purified salt) was 45.0 g. or 56.1%.

*Anal.* Calcd. for $C_7H_{10}N_4 \cdot 0.5H_2SO_4$: S, 8.04. Found: S, 8.09 (as $BaSO_4$).

**Attempted Preparation of p-Aminophenylguanidine.**—A solution containing 3.7 g. of barium hydroxide and 8.6 g. of sulfate salt in 150 cc. of water was agitated for twenty-four hours, the precipitated barium sulfate filtered off, and the filtrate evaporated to dryness under vacuum on a warm water-bath. The brown pasty residue was taken up in boiling absolute alcohol, the solution filtered hot, and a small amount of insoluble residue discarded. Upon slow evaporation of the alcohol an amorphous material deposited. This was filtered off, washed with ether and dried at room temperature in vacuo. The dry compound was light brown in color, readily soluble in cold water, and melted with decomposition at 174–178°.

In attempted purification the brown material was extracted for five days with absolute alcohol, in which only a small amount dissolved. This was surprising as the compound originally had been recovered from an alcoholic solution. The insoluble residue, after washing with ether, and drying at room temperature under vacuum, was light brown, amorphous, appeared very uniform and melted with decomposition at 182°. A second alcoholic extraction failed to raise the melting point. The brown compound (m. p. 182°) showed a strong alkaline reaction in aqueous solution, and was free of sulfate and barium.

*Anal.* Calcd. for $C_7H_{10}N_4$: N, 37.33; $C_7H_{10}N_4 \cdot 2H_2O$: N, 30.11. Found: N (Kjeldahl), 29.88.

The analytical data agreed with the theoretical nitrogen content of *p*-aminophenylguanidine dihydrate. The dry base when heated above 100° even *in vacuo* readily decomposed into ammonia and *p*-phenylenediamine.

The author wishes to thank Professor H. A. Iddles of the Department of Chemistry, The University of New Hampshire, who carried out the

[4] F. Arndt, *Ber.*, **54**, 2236 (1921).

micro analyses on the nitrate salt, and acknowledges the technical assistance of Mr. C. E. Fisher of The Lyndon Institute, Lyndon Center, Vermont. The author also thanks the American Cyanamid Company for the thiourea used in this work.

## Summary

1. The preparation of the nitrate, hydrochloride and sulfate salts of *p*-aminophenylguanidine has been described.

2. Some experimental evidence has been presented which indicates that the free base, *p*-aminophenylguanidine, has been obtained as a dihydrate.

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[CONTRIBUTION NO. 84 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

# POLYMERS FROM BENZYL CHLORIDE AND RELATED COMPOUNDS

BY RALPH A. JACOBSON

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The formation of an insoluble hydrocarbon by the action of aluminum chloride on benzyl chloride was observed many years ago by Friedel and Crafts.[1] In the same year Gladstone and Tribe[2] obtained related materials from benzyl chloride by the action of a copper–zinc couple, and previous to these observations a similar product had been obtained by means of copper.[3] Although the formation of polymeric substances from benzyl chloride has since been referred to in a number of instances,[4] little information is available concerning the nature or properties of the polymers. Insoluble amorphous products have sometimes been obtained while in other instances the polymers have been soluble resins, yet the experimental conditions pertinent to the formation of one or the other have not been defined. In view of this situation and as part of a general study of polymeric substances, the earlier work has been repeated and extended. The study has also included the polymerization of *p*-bromobenzyl chloride

[1] Friedel and Crafts, *Bull. soc. chim.*, **43**, 53 (1885).

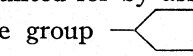
[2] Gladstone and Tribe, *J. Chem. Soc.*, **47**, 448 (1885).

[3] Zincke, *Ber.*, **2**, 739 (1869).

[4] Schramm, *ibid.*, **26**, 1706 (1893); Radziewanowski, *ibid.*, **27**, 3237 (1894); Auger, *Bull. soc. chim.*, [3] **21**, 562 (1899); Mailhe, *Chem. Z.*, **29**, 464 (1905); Lavaux and Lombard, *Bull. soc. chim.*, [4] **7**, 541 (1910); Lavaux, *Ann. chim.*, [8] **20**, 488 (1910); von Braun and Deutsch, *Ber.*, **45**, 1267 (1912); Badische Anilin und Soda-Fabrik, German Patent 280,595, Issued November 21, 1914, *Chem. Zentr.*, **86**, 71 (1915); Korczynski, Reinholz and Schmidt, *Roczniki Chem.*, **9**, 731 (1929); *Chem. Abstracts*, **24**, 1858 (1930); Ushakov and Kon, *Zhur. Prikladnoĭ Khim.*, **3**, 69 (1930); *Chem. Abstracts*, **24**, 3796 (1930).

under similar conditions, and the formation of polymers from *p*-dibromobenzene and *p*-xylylene bromide by means of the Wurtz reaction.

When benzyl chloride was polymerized by aluminum chloride, two products were obtained in varying amounts depending upon the experimental conditions. One of these was an infusible, insoluble, amorphous solid and the other a soluble, brown resin which softened and melted at 70–85°. The latter was soluble in all proportions in chloroform, carbon disulfide, and aromatic hydrocarbons, but insoluble in alcohols, ketones, and aliphatic hydrocarbons. Although the soluble polymer exhibited typical resin characteristics, it was not compatible with pyroxylin, cellulose acetate, polyvinyl acetate, polyvinyl chloride, drying oils, or with glyptal resins. Molecular weight determinations in benzene by the ebullioscopic method gave for different lots of resin, values varying from 1260 to 2250. It is of interest that an amount of aluminum chloride as small as 0.005 mole per mole of benzyl chloride was sufficient to effect polymerization within a few minutes. Under these conditions the insoluble amorphous polymer and the resin were obtained in a ratio of about 2.5 to 1. When the quantity of aluminum chloride was increased tenfold, polymerization occurred more vigorously to yield the insoluble polymer as the main product and only a small amount of the resin. With 0.004 mole of ferric chloride the polymerization proceeded slowly and the fusible soluble resin was the main product. The polymerization proceeded still more slowly with stannic chloride to yield as the only product, a soluble resin having a molecular weight of about 1300 to 1500.

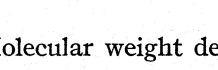
Chemically, both the soluble and the insoluble polymers were hydrocarbons having the empirical formula $C_7H_6$. The only exception was the resin obtained by means of stannic chloride, which contained a small amount of chlorine. In view of the experimental conditions employed, it is surprising that the reaction should yield exclusively materials of high molecular weight.[4a] The formation of considerable quantities of 9,10-dihydroanthracene by the intercondensation of two benzyl chloride molecules might reasonably be expected especially since such a condensation would involve the formation of a six-membered ring. The properties of the soluble polymers can be accounted for by assuming that they are hydrocarbon chains containing the group  —$CH_2$— as the structural unit. It is likely that coupling occurs mainly in the position para to the methylene group, since the para isomer is usually obtained in larger amounts than the ortho or meta isomers when the Friedel–Crafts reaction is applied to toluene, diphenyl and related compounds.[5] Undoubtedly

[4a] Since this paper was submitted, an article by Wertyporoch and Farnik has appeared [*Ann*, **491**, 265 (1931)] in which the isolation of small amounts of tolyl benzyl chloride is reported.

[5] Gattermann and Koch, *Ber.*, **30**, 1622 (1897); Limpricht, *Ann.*, **312**, 92 (1900);

occasional ortho and perhaps meta linkages may occur to render the chains unsymmetrical. The properties of the insoluble and infusible polymers can be explained by assuming a three-dimensional structure as in the case of Bakelite C.[6]

While no information concerning the number of structural units in the hydrocarbon chain of the insoluble polymer could be obtained, the average number of $C_7H_6$ groups in the chains of the soluble resins varied from 14 to 29, as indicated by molecular weight determinations. Reliable information concerning the arrangement of the units in the chain could not be secured on account of the resistance of the polymers to reagents. Attempts to oxidize the products revealed a high degree of stability, such oxidizing agents as potassium permanganate and potassium dichromate being without effect. By the action of nitric acid on the soluble polymer, an infusible resin containing nitrogen was obtained, but the presence of nitro groups could not be established. Chromium trioxide in boiling acetic acid gave products corresponding approximately to the structure $(—C_6H_4-COC_6H_4CO—)_x$. However, the presence of ketone groups could not be demonstrated by the usual methods. The action of bromine upon the soluble polymer yielded a product containing one bromine atom for two $C_7H_6$ groups.

The main product from the reaction of aluminum chloride and *p*-bromobenzyl chloride in carbon disulfide was an insoluble and infusible polymer. This was accompanied by a small amount of resin similar in solubility characteristics to the benzyl resins. When ferric chloride was used as the catalyst, the entire product was a soluble resin. Both the soluble and insoluble polymers were halogenated hydrocarbons having the empirical formula $(C_7H_5Br)_x$, for which the structural unit would be the group  . Molecular weight determinations gave values from 2000 to 2600, indicating that the chains of the soluble resins averaged from 12 to 15 units. A similar soluble halogenated hydrocarbon, $(C_7H_5Br)_x$, was obtained by Boeseken[7] although the molecular weight was not determined. As in the case of the benzyl chloride polymers, the chains would be unsymmetrical, since linkage through the position meta to the methylene group is also possible. The polymers were not readily attacked by oxidizing agents but bromination of the soluble resin yielded a product containing one bromine atom per $C_7H_5Br$ group.

Liebermann and Zsuffa, *Ber.*, **44**, 857 (1911); Lawrence, THIS JOURNAL, **43**, 2577 (1921); Blanc, *Am. Perfumer*, **17**, 541 (1923); *Perfumery Essent. Oil Record*, **14**, 40 (1923); Stephen, Short and Gladding, *J. Chem. Soc.*, **117**, 510 (1920); Huston, THIS JOURNAL, **46**, 2775 (1924).

[6] Carothers, *Chem. Reviews*, **8**, 353 (1931).

[7] Boeseken, *Rec. trav. chim.*, **23**, 100 (1904).

By the action of sodium upon *p*-dibromobenzene and upon *p*-xylylene bromide, polymeric substances were also obtained. The polymer obtained from *p*-dibromobenzene and sodium in ether was readily soluble in aromatic hydrocarbon solvents and contained about 19.5% halogen. A polymer of similar properties but containing only 12.7% halogen was formed when the reaction was conducted in toluene. The chains in each case probably consist of phenylene groups and terminate at both ends in bromine atoms. The formulas $C_{48}H_{32}Br_2$ and $C_{84}H_{56}Br_2$ are indicated by the analytical data and molecular weights, and compare favorably with the formulas, $C_{48}H_{32}Br_2$ and $C_{78}H_{52}Br_2$, assigned by Goldschmidt[8] to two polymers obtained by the reaction of *p*-dibromobenzene with sodium in ether[9] for three and five days, respectively. From *p*-xylylene bromide, an infusible and insoluble polymer having the empirical formula $(C_8H_8)_x$ was obtained. From the method of preparation and the properties of this polymer, it is certain that structurally it consists of long chains of —$CH_2$⟨⟩$CH_2$— groups. The absence of accompanying soluble polymers of lower molecular weight is unexpected since in an analogous reaction between decamethylene bromide and sodium,[10] an entire series of hydrocarbons was obtained. An infusible polymer of similar appearance and properties was obtained from *p*-xylylene bromide and magnesium, though this product contained 4.72% bromine. Assuming that bromine is present at both ends of the chain, the chains of this polymer would consist of 31 $C_8H_8$ groups and the polymer would have a molecular weight of about 3200.

## Experimental

**Polymerization Experiments.**—A mixture of 51 g. (0.4 *M*) of benzyl chloride and 0.267 g. (0.002 *M*) of powdered aluminum chloride reacted at room temperature. Evolution of hydrogen chloride began at once and within twenty minutes the mass had become solid. The yellow product was placed in boiling dilute hydrochloric acid for fifteen minutes, washed with hot water, and finally extracted several times each with alcohol, ether and acetone. The pale yellow granular solid was infusible, and practically insoluble in the common organic solvents; yield, 16.5 g.

*Anal.* Calcd. for $(C_7H_6)_x$: C, 93.33; H, 6.67. Found: C, 92.83, 93.09, 93.32; H, 6.97, 7.15, 6.86; Cl, none.

The solvents used in the extraction of the above polymer were combined and distilled. Following the recovery of 10.5 g. of benzyl chloride, there remained in the distilling flask 6.5 g. of a transparent brittle light brown resin (m. p. 70–80°), which was soluble in aromatic hydrocarbons in all proportions, but insoluble in aliphatic hydrocarbons.

[8] Goldschmidt, *Monatsh.*, **7**, 42 (1886).

[9] Riese [*Ann.*, **164**, 161 (1872)], also obtained a polymer by the interaction of *p*-dibromobenzene and sodium. Kraus and White [THIS JOURNAL, **45**, 768 (1923)], obtained a tar from *o*-dichlorobenzene and sodium in liquid ammonia.

[10] Carothers, Hill, Kirby and Jacobson, *ibid.*, **51**, 5279 (1930).

*Anal.* Calcd. for $(C_7H_6)_{14}$: C, 93.33; H, 6.67; mol. wt. 1260. Found: C, 93.16, 92.16; H, 6.94, 7.01; mol. wt. 11.91, 1241 (cryoscopic in benzene).

When the amount of aluminum chloride was increased tenfold, the reaction proceeded more vigorously and yielded a larger quantity of the insoluble polymer. Other factors such as the presence of solvents and the nature of the catalyst also influenced the reaction. The results of a number of experiments with benzyl chloride and *p*-bromobenzyl chloride under varying conditions are shown in the accompanying table. The products obtained by treating *p*-dibromobenzene and *p*-xylylene bromide with sodium are also indicated.

TABLE I

PREPARATIONAL AND ANALYTICAL DATA

| Compound | Condensing agent Mole | Condensing agent | Mole | Solvent | Mole | Insoluble polymer, g. | Soluble polymer, g. | M. p., °C. |
|---|---|---|---|---|---|---|---|---|
| A Benzyl chloride | 0.4 | $AlCl_3$ | 0.02 | ... | .. | 33.5 | 2.0 | 70–80 |
| B Benzyl chloride | .4 | $AlCl_3$ | .002 | $CS_2$ | 0.83 | 12.0 | 6.5 | 80–85 |
| C Benzyl chloride | .4 | $FeCl_3$ | .0041 | $CS_2$ | .83 | 1.5 | 22.0 | 84–88 |
| D Benzyl chloride | .4 | $SnCl_4$ | .0019 | ... | ... | None | 28 | 68–75 |
| E *p*-Bromobenzyl chloride | .1 | $AlCl_3$ | .01 | $CS_2$ | .42 | 8.0 | 2.0 | 120–135 |
| F *p*-Bromobenzyl chloride | .1 | $FeCl_3$ | .004 | $CS_2$ | .83 | None | 15.5 | 125–135 |
| G *p*-Dibromobenzene | .1 | Na | .22 | Ether | .5 | None | 4.8 | Infusible |
| H *p*-Dibromobenzene | .1 | Na | .22 | Toluene | .47 | None | 6.0 | Infusible |
| I *p*-Xylylene bromide | .1 | Na | .44 | Toluene | 1.6 | 20 (infusible) | None | |

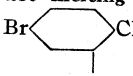
| | Analyses C | | H | | Halogen | Mol. wt. b. p. in benzene | |
|---|---|---|---|---|---|---|---|
| A Ins. sol. | 92.70 | 93.05 | 7.08 | 6.30 | ..... | | |
| A Sol. pol. | 92.89 | 92.85 | 6.62 | 6.52 | ..... | 2277 | 2304 |
| B Ins. sol. | 93.13 | 93.35 | 6.79 | 7.07 | ..... | | |
| B Sol. pol. | 93.18 | 93.39 | 6.72 | 6.87 | ..... | 1680 | 1727 |
| C Ins. sol. | 92.92 | 92.89 | 7.06 | 7.08 | ..... | | |
| C Sol. pol. | 92.94 | 92.81 | 6.87 | 6.68 | ..... | 1764 | 1789 |
| D Sol. pol. | 92.02 | 92.18 | 6.58 | 6.47 | Cl, 1.39, 1.40 | 1514 | 1529 |
| E Ins. pol. | 54.83 | 54.81 | 3.56 | 3.64 | Br, 47.66, 47.84 | | |
| E Sol. pol. | 56.70 | 56.38 | 3.73 | 3.52 | Br, 45.39, 45.44 | 1977 | 2158 |
| F Sol. pol. | 54.37 | 54.41 | 3.24 | 3.38 | Br, 52.35, 52.35 | 2420 | 2600 |
| G | 74.09 | 74.12 | 4.19 | 4.45 | Br, 19.21, 19.58 | | |
| H | 81.36 | 81.53 | 4.37 | 4.62 | Br, 12.58, 12.88 | | |
| I | 91.94 | 91.95 | 8.46 | 7.96 | | | |

**Oxidation and Bromination Experiments.**—The benzyl resin was recovered unchanged when treated with potassium permanganate or with potassium dichromate. Strong nitric acid at 100° converted the resin into a hard infusible mass containing nitrogen but the presence of nitro groups could not be confirmed by qualitative tests. Reaction of the resin with chromium trioxide in boiling acetic acid yielded a resin (m. p. 175–185°) whose analysis indicated the presence of ketone groups. However, the presence of these could not be established by the usual tests. Bromination of the benzyl resin in sunlight yielded a product containing one bromine atom per two $C_7H_6$ groups.

*Anal.* Calcd. for $(C_6H_4CO)_x$: C, 80.77; H, 3.85. Found: C, 79.11, 79.23; H, 4.08, 4.29.

*Anal.* Calcd. for $(—C_6H_4CHBrC_6H_4CH_2—)_x$: C, 64.87; H, 4.24; Br, 30.89. Found: C, 65.81, 65.97; H, 4.38, 4.58; Br, 30.98, 31.04.

Attempts to oxidize the *p*-bromobenzyl resin with chromium trioxide, permanganate and with sodium dichromate were unsuccessful. Bromination in sunlight gave a product melting at 225–235° the analysis of which indicated one bromine atom per




group.

*Anal.* Calcd. for $(—C_7H_4Br_2—)_x$: Br, 64.40. Found: Br, 63.20, 62.82.

## Summary

1. Polymerization of benzyl chloride has been effected by small amounts of aluminum chloride, ferric chloride, and stannic chloride. Aluminum chloride yielded mainly an insoluble hydrocarbon $(C_7H_6)_x$ and a small amount of soluble resin having the same empirical formula. The proportions of these were reversed when ferric chloride was employed, while stannic chloride yielded entirely the soluble polymer. The molecular weights of the soluble resin varied from 1260 to 2250. The hydrocarbon chains were not readily attacked by oxidizing agents.

2. Polymerization of *p*-bromobenzyl chloride has been effected under similar conditions and with comparable results. The structural unit of both the insoluble and soluble polymers was $C_7H_5Br$ and the molecular weights of the resin varied from 1300 to 1500.

3. Polymers have been obtained from *p*-dibromobenzene and *p*-xylylene bromide by means of the Wurtz reaction. The former yielded a soluble polymer whereas the latter gave an infusible insoluble polymeric hydrocarbon having the empirical formula $(C_8H_8)_x$.

WILMINGTON, DELAWARE

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[201ST CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

# THE CHEMISTRY OF LIGNIN. VI. THE DISTILLATION OF ALKALI LIGNIN WITH ZINC DUST IN AN ATMOSPHERE OF HYDROGEN

BY MAX PHILLIPS AND M. J. GOSS

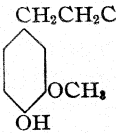
RECEIVED OCTOBER 29, 1931 PUBLISHED APRIL 6, 1932

In a previous communication by one of us[1] the results of some experiments on the distillation of lignin with zinc dust in an atmosphere of hydrogen were given. Among the products of distillation obtained were catechol, guaiacol, and a phenolic methyl ether which gave a 3,5-dinitrobenzoyl derivative melting at 110°.

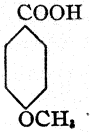
The present paper gives the results of a further study of the same reaction. In addition to the degradation products mentioned above, we have succeeded in isolating a phenolic compound which has been identified as 1-*n*-propyl-3-methoxy-4-hydroxybenzene (I). When oxidized with

[1] Phillips, THIS JOURNAL, **53**, 768 (1931).

aqueous potassium permanganate the "neutral fraction" of the oily distillate from the zinc dust distillation of the lignin yielded anisic acid (II).




I




II

The isolation of these two compounds as degradation products of lignin indicates that there are in the lignin molecule in addition to other possible units at least two aromatic nuclei or those which can be readily converted into aromatic nuclei. One nucleus has a side chain having at least three carbon atoms in addition to a methoxyl group and a hydroxyl group in the positions meta and para, respectively, to the side chain. The other nucleus has a side chain and a methoxyl substituent para to the side chain.

## Experimental

The lignin[2] was distilled with zinc dust at a maximum temperature of 400° in the type of apparatus and under the conditions previously described.[3] A total of 250 g. of lignin was distilled, and the yield of oil amounted to 37.5 g. (=15% of the weight of the lignin used). The oil obtained was dissolved in ether. This solution was extracted with 5% aqueous sodium hydroxide and thus resolved into an alkali-soluble fraction and an alkali-insoluble or neutral fraction. The alkali-soluble portion was acidified and the phenolic oil was steam distilled. The residue in the distilling flask was a tarry mass from which nothing definite could be isolated. The steam volatile phenols were dissolved in an equal volume of anhydrous ether, cooled with ice, and an excess of a saturated solution of potassium hydroxide in absolute alcohol was then added. After standing for about one-half hour the potassium phenolate was filtered off and washed with anhydrous ether. The potassium phenolate was dissolved in water, acidified with sulfuric acid, and the phenol was extracted with ether. The ether solution was dried over anhydrous sodium sulfate and filtered, and after removal of the ether by distillation the oily residue was distilled. The oil distilled over at 202–207°; yield 1 g. The 3,5-dinitrobenzoyl ester of this was prepared by the method previously described.[4] After two crystallizations from 95% ethanol, crystals were obtained melting at 114° (corr.). The melting point of the 3,5-dinitrobenzoyl ester of 1-*n*-propyl-3-methoxy-4-hydroxybenzene is 116° (corr.). The optical properties of the crystals melting at 114° were also found to be identical with those of the 3,5-dinitrobenzoyl ester of 1-*n*-propyl-3-methoxy-4-hydroxybenzene.

The filtrate from the solid potassium phenolate was acidified with dilute sulfuric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate and filtered and, after removal of the solvent, the residual oil was fractionally distilled. The following two fractions were obtained: (1) 196–203°, 1 g.; (2) 203–215°, 2.5 g.

**Fraction 196–203°.**—The 3,5-dinitrobenzoyl ester of this was prepared. After three crystallizations from 95% ethanol, crystals were obtained which melted sharply

[2] The lignin used in these experiments was isolated from corn cobs following the method indicated in a previous communication (Ref. 1, p. 770).

[3] Ref. 1, p. 770.

[4] Phillips and Keenan, THIS JOURNAL, **53**, 1924 (1931).

at 141° (corr.). When this substance was mixed with some pure 3,5-dinitrobenzoyl-guaiacol, the resulting mixture also melted at 141°. The optical properties of the crystals of the two preparations were also found to be identical. This fraction, therefore, consisted principally of guaiacol.

**Fraction 203–215°.**—The 3,5-dinitrobenzoyl ester was prepared and after three crystallizations from 95% ethanol it melted sharply at 116.8° (corr.). When mixed with some pure 3,5-dinitrobenzoyl ester of 1-*n*-propyl-3-methoxy-4-hydroxybenzene, no depression in the melting point was observed. The optical properties of the crystals of the ester prepared from fractions 203–215° were in every respect identical with those of the 3,5-dinitrobenzoyl ester of 1-*n*-propyl-3-methoxy-4-hydroxybenzene.

**Examination of the "Neutral Fraction."**—The ether solution which had been extracted with 5% sodium hydroxide solution was filtered and the ether distilled off. The residue was distilled in a current of steam; the distillate and the aqueous residue in the flask were extracted with ether. Both ether solutions were dried over anhydrous sodium sulfate and filtered, and the ether was removed by evaporation. A steam volatile neutral fraction (A) and a steam non-volatile neutral fraction (B) were thus obtained. The yields amounted to 7 and 3 g., respectively.

**Examination of Steam-Volatile Neutral Fraction A.**—This was distilled under ordinary pressure, and two fractions were obtained, namely, 215–230° (3.0 g.) and 230–260° (2.5 g.).

**Oxidation of Fraction 215–230° with Potassium Permanganate.**—The oil was placed in a flask which was attached to an inverted condenser. The flask was heated in a boiling water-bath and a 4% aqueous potassium permanganate solution added with stirring until no further decoloration of the permanganate solution took place. The excess of potassium permanganate was destroyed with hydrogen peroxide; the manganese dioxide was filtered off, and the alkaline filtrate was concentrated and then acidified with hydrochloric acid, whereupon a colorless crystalline precipitate was obtained. This was crystallized from dilute alcohol and colorless needles, melting at 184° (corr.), were obtained. When a portion of this crystalline substance was mixed with some pure anisic acid, the melting point of the mixture was also 184° (corr.).

*Anal.* (Methoxyl). Subs., 0.0205: AgI, 0.0317. Calcd. for $C_8H_8O_3$; $OCH_3$, 20.39. Found: $OCH_3$, 20.43.

The optical properties of the crystals of the acid melting at 184°, obtained by the oxidation of fraction 215–230°, were also found to be identical with those of anisic acid.

**Oxidation of Fraction 230–260°.**—This was oxidized with aqueous potassium permanganate according to the method previously described. The concentrated filtrate from the manganese dioxide was acidified with hydrochloric acid and, as no precipitate separated out, the solution was extracted with ether, and the ether was distilled off. The residue was crystallized from dilute alcohol, from which it separated out as needles. This was identified as anisic acid by its melting point, mixed melting point and by the optical properties of the crystals.

The steam non-volatile neutral fraction (B) was distilled under reduced pressure (9 mm.). It distilled over as a viscid oil at 180–190° from which, however, nothing definite was obtained.

**Distillation of Lignin with Zinc Dust at Low Red Heat.**—The distillations were carried out in an ordinary electrically heated combustion furnace. The combustion tube was filled in a manner similar to that used in the previous experiment. Altogether seven runs were made representing a total of 260 g. of lignin. The oil obtained in the various runs was combined and the total amounted to 28.5 g. ($\approx$10.9% of the weight of the lignin distilled).

A chemical examination of this oil was made according to the procedure given

above. In the phenolic fraction only guaiacol was identified. The "neutral" fraction on oxidation yielded an acid which was identified as anisic acid by its melting point, mixed melting point, and the optical properties of the crystals.

## Summary

1. Alkali lignin, isolated from corn cobs, was distilled with zinc dust in an atmosphere of hydrogen at a maximum temperature of 400°. The oily distillate was separated into a phenolic fraction and a "neutral" fraction. In the phenolic fraction guaiacol and 1-*n*-propyl-3-methoxy-4-hydroxybenzene were identified. The "neutral fraction" when oxidized with potassium permanganate yielded anisic acid.

2. The significance of these findings from the standpoint of the structure of lignin is briefly discussed.

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[CONTRIBUTION FROM THE PRIVATE LABORATORY OF THE AUTHOR]

# ALKYLATION OF ORANGE I. A REFUTATION

BY KARL H. T. PFISTER

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## Introduction

There has recently appeared a paper by K. H. Slotta and W. Franke,[1] entitled "Zur Konstitution der Azo-Indicatoren. I. Mitteilung: α-Naphthol-Orange" ("The Constitution of Azo Indicators. Part I. α-Naphthol Orange").

When the writer first glanced over this paper, he was struck by the novel character of it, and by the departure of the two authors from long established and often confirmed experience, concerning the constitution and certain typical properties of those azo dyes which carry a phenolic hydroxyl group in para position to the azo group. Such dyes have always been known to be very sensitive to the action of alkali, in so far as their usually yellow or orange shades are turned deep red, even by weak alkalies. It has been recognized long ago that the alkylation of the hydroxyl group renders these dyes indifferent, or to use the technical term, "fast" to alkali, and thereby makes them suitable for certain practical applications—for instance, the dyeing of textile goods.

Amongst the members of the group of azo dyes mentioned above, there is one called Alpha-Naphthol-Orange or Orange I, which is made by coupling diazotized sulfanilic acid with α-naphthol, and it is this particular dye with which the paper of Slotta and Franke deals.

It seems that relative to the alkylation of this dye, there is no reference in the chemical literature previous to the article of Slotta and Franke but

[1] Slotta and Franke, *Ber.*, **64**, 86 (1931).

there is not the least reason for presuming that this alkylation, if actually performed, should take a different course than the alkylation of other *p*-hydroxy azo dyes. The only difference which has in the past been noticed between various members of the group was the readiness with which alkylation takes place, but there has never been any doubt as to the spot which is attacked. Slotta and Franke, however, make the startling claim that the alkylation of Orange I does not produce phenolic ethers as usual but that the alkyl group becomes attached to one of the two nitrogen atoms of the azo group, and that consequently the mono alkyl derivatives of Orange I are turned red by alkali, just as Orange I itself. This claim rests on the results of some alkylation experiments which Slotta and Franke have made. They consider their interpretation of these results as a solid support of their claim although they admit that they have failed in their attempts to furnish positive experimental proof of the alkyl-nitrogen attachment. The ultimate object of the work of Slotta and Franke is the promotion of a new physico-chemical theory on the relations between indicator properties and constitution of azo dyes. For the details the reader should consult the original paper. Slotta and Franke have possibly not been aware of the sensational character of the claim derived from their alkylation experiments. It amounts to no less than the discovery of a reaction which is without parallel in the chemistry of the azo dyes, and which is contrary to fundamental conceptions of the organic dyestuff chemist. Before the latter submits to the painful process of giving up these conceptions, he will, of course, investigate the validity of the experimental proof furnished by Slotta and Franke.

This was the object of the writer in making the experiments described in the following pages.

## Experimental

The occasion demands that in the description of his basic experiments the writer must go into more detail than would ordinarily be necessary. Slotta and Franke give a rather meager account of the synthetic part of their work, while they devote more space to their physico-chemical tests and theoretical deductions.

**Methylation of Orange I.**—Slotta and Franke used only 3.3 g. of starting material for their experiment. Such an amount is rather small for this type of research, unless the investigator is certain that the reaction will take the expected course and that it will be quantitative. No such certainty existed in the case at hand. Furthermore, Slotta and Franke have worked up the reaction mass with acid, which is impractical and deceiving, as will be seen. In the following three experiments the amounts used by Slotta and Franke were multiplied by five and the reaction mass was worked up alkaline, whereas relative proportions of the reacting materials and the reaction time were exactly the same as in Slotta and Franke's experiment.[2]

[2] Ref. 1, p. 90.

**Experiment I.**—Slotta and Franke state that they have heated the reaction mixture on the water-bath but they do not record the temperature which the mass has reached. It was assumed to have been 50 to 60° because they mention this temperature in the description of another experiment on the same page.

16.5 g. (one-twentieth mole) of Orange I, free acid,[3] was put into a 250-cc. round-bottomed flask; 60 cc. of water was added and 12.5 cc. (three-twentieth mole) of caustic soda solution, 40° Bé. A deep cherry red solution resulted. To this was added within five minutes under constant shaking 15 cc. (three-twentieth mole) of dimethyl sulfate[4] in three portions. Shaking was kept up another five minutes. The mixture became thicker and slightly warm. It was then heated on the water-bath for one hour so that a thermometer inserted into the flask content registered a temperature of 50 to 60°. The mass had then assumed an acid reaction, as was to be expected. It was dissolved with a mixture of 150 cc. of water and 23 cc. caustic soda solution of 40° Bé. The resulting solution was deep cherry red, exactly like the original alkaline solution of Orange I. However, a close inspection revealed a fine suspension in the liquid. This was filtered on a Buchner funnel and the cake was washed with distilled water until the filtrate was no longer deep red but merely pale orange. The filter cake, after drying in the air, weighed 10.5 g.[5] When dissolved with 150 cc. of boiling water, a glittering mass of fine crystals separated out on standing. The microscope disclosed a uniform array of pale yellow boat-shaped individuals. These were filtered off and dried in the air, giving 8.8 g. of substance of a pronounced micro-crystalline structure, light orange in color with a distinct brownish-golden bronze.

This material[6] differs radically from the sodium salt of Orange I. It is moderately soluble in cold water and its shade (yellow in dilute solution) is not in the least changed by weak or strong alkalies (spot test on filter paper). It has, therefore, no indicator properties whatsoever.

This behavior shows convincingly that the methylation has taken the normal course and that the methyl ether of Orange I has been formed, just as such ethers are formed in analogous cases.

*Anal.* 3.1630 g. of the air-dried material weighed 2.8741 g. after heating for two hours at 120°. This loss is equivalent to two molecules of water of crystallization. Subs. (anhydrous), 0.4692: 12.6 cc. of 0.2 *N* HCl. Calcd. for $C_{17}H_{13}O_4N_2SNa$: N, 7.69. Found: N, 7.55.

For the nitrogen determination the Phelps–Daudt modification of the Kjeldahl method was used.[7]

A sharp line of discrimination between the sodium salt of Orange I and its methyl ether is drawn by the following qualities. In dilute (*e. g.*, 2%) caustic soda solution,

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[3] It is much more convenient to use 20 g. (one-twentieth of a mole) of Orange I Food Color (which contains 90% pure coloring matter in the form of the sodium salt) and consequently 8.3 cc. (two-twentieth of a mole) of caustic soda, 40° Bé. This was done in the following experiments.

[4] From Eastman Kodak Company.

[5] From the deep red filtrate an excess of concentrated hydrochloric acid precipitated tiny black needles, just as did the original solution of Orange I.

[6] It is, of course, a sodium salt since it has separated out of a sodium hydroxide solution.

[7] The method was found very reliable. It is hard to understand why most scientific research laboratories still persist in using the antiquated and cumbersome Dumas method after so elegant a method as that of Phelps and Daudt has become available (see *J. Assn. Off. Agr. Chem.*, **3**, 310 (1920).

Orange I is very readily soluble (deep red) while the ether is very nearly insoluble (filtrate practically colorless).

Another feature of the ether we will meet with in the following experiment.

**Experiment 2.**—This experiment was made in order to determine whether heating of the reaction mass on the *boiling* water-bath made any difference in the result. The experiment has led to an interesting observation.

The procedure was exactly the same as in Expt. 1 except that the thermometer in the reaction flask registered a temperature of about 90° against 50 to 60° in Expt. 1. No methyl ether could be isolated in this case.

The cause was discovered when a little sample of the pure methyl ether from Expt. 1 was boiled in a test-tube with dilute (10%) sulfuric acid. The resulting solution was turned red by alkali just as was the solution of Orange I. The acid had obviously hydrolyzed the ether.

This instability of the ether in an acid medium, especially at a higher temperature, explains why no ether was obtained in Expt. 2.

**Experiment 3.**—Experiment 2 has shown the importance of the temperature in regard to ether yield. Therefore Experiment 3 was made without application of heat in order to see whether this procedure would increase the yield over that of Experiment 1. This was found to be the case: 12.9 g. of crude[8] ether was obtained equal to 65% of the theoretical yield, against 53% in Experiment 1.

**Ethylation of Orange I.**—In their ethylation experiment[9] Slotta and Franke have boiled Orange I under reflux in alcoholic solution with caustic soda and diethyl sulfate. Their experiment was repeated and no ether whatsoever could be isolated. This result corresponds to that of methylation Experiment 2 described above. Then another experiment was made exactly analogous to the writer's methylation Experiment 3 merely substituting the equivalent amount of diethyl sulfate for the dimethyl sulfate. 10.3 g. of air-dry ether was obtained. This is a yield of about 50% of the theoretical. This material was crystallized from 200 cc. of water and yielded 7.8 g. of air-dry substance.

*Anal.* 5.1940 g. after heating for two hours at 120° weighed 4.7428 g. This loss is equivalent to two molecules water of crystallization. Subs. (anhydrous) 0.3693: 9.7 cc. of 0.2 *N* HCl. Calcd. for $C_{18}H_{15}O_4N_2SNa$: N, 7.41. Found: N, 7.38.

The ethyl ether formed a coarsely crystalline powder without brownish bronze and, therefore, of a brighter orange appearance than the methyl ether. Otherwise its properties are so similar to those of the methyl ether that they need not be especially described.

The rest of the alkylations we can deal with more briefly because the results were perfectly analogous, as was to be expected.

**Propylation and Butylation of Orange I.**—The method employed by Slotta and Franke was used, that is, boiling in alkaline alcoholic solution with *n*-propyl-*p*-toluenesulfonate or *n*-butyl-*p*-toluenesulfonate. For the sake of uniformity sodium hydroxide was substituted for the potassium hydroxide used by Slotta and Franke[10] and the reaction mass was, of course, worked up alkaline after evaporation of the alcohol. The yields of crude ether were about 57 and 65% of the theoretical, respectively.

**Hexylation of Orange I.**—Again the same method as that of Slotta and Franke was used, namely, boiling in alkaline alcoholic solution with *n*-hexyl bromide. The ether yield was about 44% of the theoretical.

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[8] By "crude" is meant "not recrystallized" but the preparations were washed free from unchanged Orange I and from mineral salts.

[9] Ref. 1, p. 91, No. 3.

[10] Slotta and Franke use sodium hydroxide in some experiments and potassium hydroxide in others.

## Résumé of the Experimental Work of the Writer and Interpretation of the Work of Slotta and Franke

The experiments described above have brought to light the facts in regard to the alkylation of Orange I when employing the methods of Slotta and Franke.

It has been found that the ethers of Orange I can be isolated to an extent of between 44 to 65% of the theoretical and that these ethers are stable to alkali but readily hydrolyzed by acids.

The alkaline filtrates from the ethers gave on precipitation with acid dark crystalline precipitates which displayed not a single feature which would warrant the conclusion that they represented anything else but starting material, that is, the free acid of Orange I.

The sensitiveness of the ethers of Orange I to acid is quite remarkable. Simple test-tube experiments give the following picture. While boiling with dilute mineral acid effects rapid hydrolysis of the ethers, a gradual hydrolysis takes place on mere standing with the acid and even with weak acids like acetic acid. It is, therefore, impossible to prepare the free color acids of the ethers in a pure state.

These facts put us now in a position to determine precisely what has taken place in the work of Slotta and Franke. Slotta and Franke have completely overlooked the formation of the ethers. They have treated the reaction mass of all their experiments with hydrochloric acid. They have, therefore, hydrolyzed the ethers which had been formed and finally they have had nothing in hand but more or less pure starting material.

Analytical evidence that acid treatment (even cold) of the reaction mass leads merely back to the starting material is furnished by the following experiment.

**Experiment.**—Butylation of Orange I, following the method used by Slotta and Franke in every respect (but multiplying the amounts by three), treatment with acid, thorough purification of the product and determination of the nitrogen.

The acid treatment and the purification were done without application of heat; 9.9 g. of free acid of Orange I was dissolved with 150 cc. of ethanol (92%) and 3.6 g.[11] of potassium hydroxide (sticks, by alcohol). Then 13.8 g. of *n*-butyl-*p*-toluenesulfonate was added. This solution was kept gently boiling on the water-bath under reflux for four hours. Then it was allowed to cool and was filtered on a Buchner funnel. The cake was pulped up in a mortar with 60 cc. of dilute (10%) sulfuric acid.[12] The pulp was then filtered and washed free from sulfuric acid with dilute hydrochloric acid. Then it was dissolved with ethanol and reprecipitated with hydrochloric acid. The material was filtered on the Buchner funnel, washed with ether, dried in a potassium hydroxide vacuum desiccator and then exposed to the air for a few hours; yield, 6 g.

[11] The figure of 0.2 g. in *Ber.*, p. 92 No. 4, 5 and 6 is a typographical error. It should read 1.2 g.

[12] It is always advisable to use sulfuric acid in order to liberate sulfonic acids from their salts, because there are examples in the literature when hydrochloric acid has done the work incompletely.

*Anal.* The substance was rendered anhydrous by heating for two hours at 130 to 140°.[13] 2.8328 g. was thus obtained from 3.1430 g. of air-exposed material. Subs. (anhydrous), 0.3467: 10.5 cc. of 0.2 *N* HCl; 0.3892: 11.8 cc. of 0.2 *N* HCl. Calcd. for $C_{16}H_{12}O_4N_2S$ (free acid of Orange I): N, 8.54. Found: N, 8.50, 8.51.

The loss of water on drying at 130 to 140° (see above) corresponds to two molecules of water of crystallization. In the air this water is taken up again. The figure obtained for the nitrogen content confirms the non-existence of the N-alkyl derivatives of Slotta and Franke.[14]

## Summary

1. The alkylation of Orange I takes a normal course.

2. The theoretical deductions of Slotta and Franke rest on a false foundation and are, therefore, of no value.

[13] Below this temperature the water of crystallization is but incompletely removed.

[14] The analytical figures given in this paper have been determined by Mr. Daniel Sassi.

SUMMIT, NEW JERSEY

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SHARP AND DOHME, INC.]

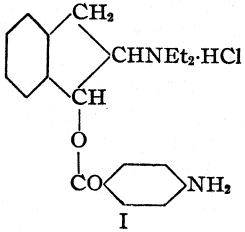
# AMINO ALCOHOLS. VIII. BENZOIC ESTERS OF ARYLALKANOLAMINES

BY WALTER H. HARTUNG, JAMES C. MUNCH AND ERNEST B. KESTER

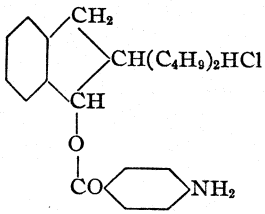
RECEIVED NOVEMBER 3, 1931 PUBLISHED APRIL 6, 1932

In the administration of local anesthetics such as procaine, epinephrine is often given simultaneously. The purpose of the latter is to constrict the blood vessels and thus prevent too rapid absorption of the desensitizing agent and to localize the anesthesia produced.[1] The ideal anesthetic would combine in a single molecule, and in proper ratio, both the desensitizing and vaso-constricting actions.

Attempts to prepare such a compound have previously been made. Marvel and du Vigneaud[2] prepared two α-hydroxyhydrindene derivatives (I and II) and phenylprocaine (III). None of the compounds had any pressor action, and I and II showed only a very slight anesthetic




I

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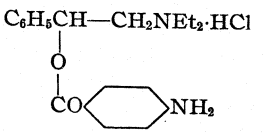


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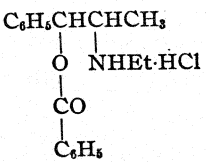
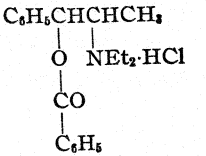
[1] Sollmann, "Manual of Pharmacology," Saunders, Philadelphia, 1926, 3d ed., p. 329; Hatcher and Eggleston, *J. Pharmacol.*, **8**, 385 (1916); Eggleston and Hatcher, *ibid.*, **13**, 433 (1919).

[2] Marvel and du Vigneaud, THIS JOURNAL, **46**, 2093 (1924).

action. Kubota[3] found that allocaines S (IV) and A (V) are strongly anesthetic and that their effect on the circulatory system was to produce



Allocaine S
IV



Allocaine A
V

a primary fall in blood pressure followed by a rise to above normal. It will be observed that they contain the linkage $ArCOOC\overset{|}{\underset{|}{C}}CN=$, an anesthesiophore group, and hence each might be expected to possess local anesthetic action. Each substance also contains a phenylethanolamine skeleton, $C_6H_5CH\overset{|}{\underset{O-}{CN}}=$, a favorable condition for pressor activity; although there is still no available evidence regarding the pressor effect of the β-aminohydrindene residues of I and II. However, one would hardly expect these substances to have much (if any) effect on the circulation, even if no allowance is made for the effect on the pressor activity produced by benzoylation of the alcoholic hydroxyl, because the alkyl groups substituted on the amino nitrogen are of such a character and magnitude as to influence adversely the pressor action.[4] Chen, Wu and Henriksen and Schaumann conclude that, in general, the primary amines of the ephedrine type are more active and less toxic than the alkylated amines. Accordingly primary amines corresponding to III, IV and V ought to preserve maximum pressor activity unless it is destroyed by esterification.

Wolfheim[5] has prepared the benzoic ester of phenylethanolamine (VI) but he made no mention of its physiological properties. In the light of our results we should expect it to be both a pressor and anesthetic. Recently Tiffeneau described the benzoic ester of phenylbutanolamine (VIII) as approaching cocaine in anesthetic potency, results which we have verified.[6] Tiffeneau made no mention of other physiological properties and probably it would not be a pressor, since the unesterified phenylbutanolamine is relatively inactive on the circulatory system.[4b,7]

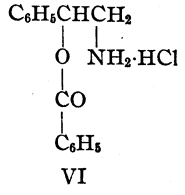
[3] Kubota, *J. Pharmacol.*, **12**, 361 (1919).

[4] (a) Barger and Dale, *J. Physiol.*, **41**, 19 (1910); (b) Chen, Wu and Henriksen, *J. Pharmacol.*, **36**, 363 (1929); (c) Schaumann, *Arch. exptl. Path. Pharmakol.*, **157**, 114 (1930); (d) Ehrhart, *Metallbörse*, **20**, 1800 (1930).

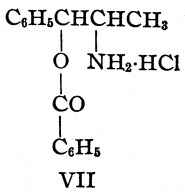
[5] Wolfheim, *Ber.*, **47**, 1440 (1914).

[6] Lévy, "Essais et Dosages Biologiques des Substances Medicamenteuses," Masson et Cie, Paris, 1930, p. 132.

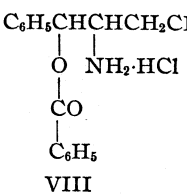
[7] Hartung, Munch, Deckert and Crossley, THIS JOURNAL, **52**, 3317 (1930).



VI



VII



VIII

To determine the effect of esterification of the alcoholic hydroxyl group of an active pressor, we prepared and examined the benzoic ester of phenylpropanolamine (VII). Pharmacological tests with this compound indicate that as an anesthetic it approaches cocaine in potency, and also that it produces a rise in blood pressure when given intravenously to anesthetized dogs. So far as the authors are aware this is the first compound with a demonstrated pressor and anesthetic action. The only other compound which might be considered as having a similar pharmacodynamic behavior is cocaine.[8] Given in small doses, it selectively stimulates the vaso-motor center and also sensitizes the sympathetic nervous system to the action of the epinephrine in circulation.[9] Large doses paralyze the center, causing a marked fall in blood pressure and leading to collapse.

In Table I is given a summary of the behavior of the benzoic ester of phenylpropanolamine hydrochloride; other active substances are included to permit ready comparison.

TABLE I

COMPARATIVE PHYSIOLOGICAL BEHAVIOR

| Compound as HCl salt | M. L. D. mg./kg. intravenous to rabbits | Local anesthesia Dogs subcutaneous mg./dog | Local anesthesia Rabbit cornea minutes duration after 1 mg. | Relative pressor action |
|---|---|---|---|---|
| Benzoic ester of phenylpropanolamine | 20 | 20 | 13 | 1 |
| Phenylpropanolamine | 75 | 0 | 0 | 10+ |
| Cocaine | 7.7[b] | 6[a] | 30 | See text |
| Procaine | 30[b] | 70[a] | 30 | |

[a] Munch, "Bioassays," Williams and Wilkins Co., Baltimore, Md., 1931, p. 65.
[b] Roth, Hygienic Lab. Bull., **109**, 43 (1917).

## Synthesis

The benzoic ester of phenylpropanolamine hydrochloride was prepared after the method described by Wolfheim[5] for the synthesis of esters of phenylethanolamine. This procedure is indicated as follows

[8] Sollmann, Ref. 1, p. 333.

[9] Meyer and Gottlieb, "Experimental Pharmacology," Lippincott, Philadelphia, 1926, p. 139; Paulsson, "Heffters Handbuch der Experimentelle Pharmakologie," Julius Springer, Berlin, 1920, Vol. II, p. 138.

$$C_6H_5CHClCH(CH_3)NH_2HCl \xrightarrow{C_6H_5COCl} C_6H_5CHClCH(CH_3)NHCOC_5H_6 \xrightarrow[(ROH)]{HOH} \begin{array}{l} C_6H_5CHCH(CH_3)NH_2HCl \\ \quad | \\ \quad O \\ \quad | \\ \quad COC_6H_5 \end{array} \xrightarrow{NH_3} C_6H_5CHOHCH(CH_3)NHCOC_6H_5$$

**Phenyl-1-amino-2-chloro-1-propane,** as its hydrochloride, has already been described.[10]

**Phenyl-1-chloro-1-benzoylamino-2-propane.**—Eight and one half grams of the phenylaminochloropropane hydrochloride was shaken with a mixture of 17 g. of benzoyl chloride, 90 ml. of water, 90 ml. of ether and 90 ml. of a 10% solution of sodium hydroxide. After the reaction had ceased the ethereal layer was drawn off and allowed to evaporate; the crystalline residue was purified by forcing it out of benzene solution with excess ligroin; in this manner 10.2 g. (calcd. 11.3 g.) of the N-benzoyl product was obtained. It began to sinter at 122° and melted at 125° (corr.).

*Anal.* Calcd. for $C_6H_5CHClCH(CH_3)NHCOC_6H_5$: N, 5.12. Found: N (Kjeldahl), 4.81.

**Benzoic Ester of Phen lpropanolamine Hydrochloride.**—The most satisfactory procedure for rearranging the N-benzoyl derivative just described was to dissolve 5.8 g. of it in a solution of 40 ml. of *sec.*-butyl alcohol and 5 ml. of water; this solution was then heated in a beaker on an electric hot-plate until it had evaporated to about half its original volume and was then diluted with excess ether (isopropyl ether was found highly satisfactory); this forced out 3.4 g. of crystals. By evaporating the mother liquors and repeatedly boiling the residues in the dilute *sec.*-butyl alcohol and forcing out with ether, it was possible to obtain an ultimate yield of 72% of the ester. The crystals were purified by forcing out of an absolute alcoholic solution with ether; m. p. 208° (corr.).

*Anal.* Calcd. for $C_6H_5CH(OCOC_6H_5)CH(CH_3)NH_2{\cdot}HCl$: Cl, 12.16. Found: Cl (as AgCl), 11.86.

This ester is stable in solution only in the form of its salt. An aqueous solution of the hydrochloride treated with ammonia causes the benzoyl group to shift from the oxygen to the nitrogen, and the N-benzoyl derivative of phenylpropanolamine precipitates, m. p. 142-143°.[11] This new rearrangement was to be expected, for Wolfheim observed a parallel behavior with his ester.

After the experimental work had been completed it was observed that Kanao[12] had already described a benzoic ester of phenylpropanolamine. He obtained his product by boiling N-benzoyl-nor-*dl*-ephedrine, m. p. 143° (the N-benzoyl derivative of phenylpropanolamine) with concentrated hydrochloric acid, which caused the benzoyl group to shift from the nitrogen to the oxygen, and the resulting ester (as hydrochloride) melted at 220°. When this was treated with ammonia the benzoyl shifted back onto the nitrogen, just as one would expect, and the N-benzoyl compound reformed. However, this time it did not melt at 143°, as did the original

[10] Hartung and Munch, THIS JOURNAL, **53**, 1875 (1931).

[11] Schmidt, *Arch. Pharm.*, **255**, 147 (1917).

[12] Kanao, *J. Pharm. Soc. Japan*, **48**, 1070 (1928); German abstract, *ibid.*, p. 145.

material, but at 128°. By comparing the ester and the final N-benzoyl substance with known products Kanao was able to identify both as derivatives of nor-*dl*-$\psi$-ephedrine. In other words, in all this process phenylpropanolamine had undergone a shift in configuration and into the pseudo form. From his results Kanao was led to believe that the ester can exist only when the amino alcohol is in this configuration. While we have as yet made no studies with the possible stereoisomers of our compounds, it would appear that our ester is of the nor-ephedrine type, for not only has it a melting point different from that found by Kanao, but the amide resulting from the rearrangement of the ester (m. p. 142–143°) is the N-benzoyl derivative of nor-*dl*-ephedrine.

## Summary

1. The synthesis of the benzoic ester of phenylpropanolamine hydrochloride has been described. This synthesis presumably does not result in isomerization into the pseudo configuration.

2. This ester is structurally related to pressors and anesthetics.

3. Benzoylation of the alcoholic hydroxyl conferred anesthetic properties but caused a decrease to a tenth or less of the pressor potency.

4. This is the first compound to possess a demonstrated pressor and anesthetic action.

PHILADELPHIA, PENNSYLVANIA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# NITROSO COMPOUNDS. I. (PRELIMINARY PAPER.) THE PREPARATION AND REDUCTION OF CERTAIN NITROSO KETONES

BY JOHN G. ASTON, DAVID F. MENARD AND M. GLENN MAYBERRY

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## Introduction

The present paper deals with the preparation of $\alpha$-nitroso ketones of the type, $(CH_3)_2C(NO)COCH_2R$, by the action of ethyl nitrite upon the corresponding ketones. The reduction of these $\alpha$-nitroso ketones has also been studied with quite unexpected results.

The direct nitrosation of ketones upon an $\alpha$-methylene group is a general reaction

$$RCH_2COR' + R''ONO \xrightarrow[C_2H_5ONa]{HCl} RC(=NOH)COR' + R''OH$$

The product of nitrosation in such cases is invariably the oxime.[1]

[1] Claisen and Manasse, *Ber.*, **22**, 526 (1889); Ponzio and DeGaspari, *J. prakt. Chem.*, [2] **58**, 392 (1896).

In order to obtain a stable true α-nitroso ketone, nitrosation must occur on a carbon atom with but one hydrogen atom; 4-nitrosomenthone has been prepared by the action of amyl nitrite and hydrochloric acid on menthone.[2] Simultaneously cleavage occurs between the nitroso substituted α-carbon and the ketone group, yielding 3,7-dimethyl-6-oximinooctanoic acid.[3]

Methyldesoxybenzoin is cleaved in a similar manner by the action of nitrous acid but in this case the intermediate nitroso compound is not obtained.[4]

$$C_6H_5COCH(C_6H_5)CH_3 + HNO_2 \longrightarrow C_6H_5COOH + C_6H_5C(=NOH)CH_3$$

## Discussion of Results

When ketones of the type $(CH_3)_2CHCOCH_2R$ are treated with an equivalent quantity of ethyl nitrite in the presence of hydrochloric acid at about 50° it is possible to isolate the bimolecular true nitroso compounds. In the case of methyl isopropyl ketone a 24% yield of methyl α-nitroso-isopropyl ketone (I) was obtained.

$$2(CH_3)_2CHCOCH_3 + 2HNO_2 \longrightarrow 2H_2O + [(CH_3)_2C(NO)COCH_3]_2$$
(I)

No product corresponding to direct nitrosation on the methyl group was found. Evidence for a cleavage as in the case of methyldesoxybenzoin was obtained by the isolation of methylglyoxime which had apparently been formed by further nitrosation of the resulting acetoxime.

$$(CH_3)_2C(NO)COCH_3 + H_2O \longrightarrow (CH_3)_2C{=}NOH + CH_3COOH \xrightarrow{HNO_2} CH_3C(=NOH)CH{=}NOH$$

In the case of ethyl isopropyl ketone a yield of 6.8% of ethyl α-nitroso-isopropyl ketone (II) was obtained along with 27% of α-isonitrosoethyl isopropyl ketone (III)

$$2(CH_3)_2CHCOCH_2CH_3 + 2HNO_2 \longrightarrow 2H_2O + [(CH_3)_2C(NO)COCH_2CH_3]_2$$
(II)

$$(CH_3)_2CHCOCH_2CH_3 + HNO_2 \longrightarrow H_2O + (CH_3)_2CHCOC(=NOH)CH_3$$
(III)

Both α-nitrosoisopropyl ketones were bimolecular, and only upon heating their solutions in various solvents did the characteristic blue color of the monomolecular form slowly appear. The blue color disappeared again on cooling. The bimolecular form is thus quite stable and it is perhaps for this reason that these compounds withstand cleavage during their formation. That we are dealing with a true nitroso group is evident from the doubling up of the molecule and the appearance of the blue color, characteristic of monomolecular true nitroso compounds.

[2] Baeyer and Manasse, *Ber.*, **27**, 1912 (1894); Baeyer, *ibid.*, **28**, 652, 1586 (1895).

[3] See also Clarke, Lapworth and Wechsler, *J. Chem. Soc.*, **93**, 30 (1908).

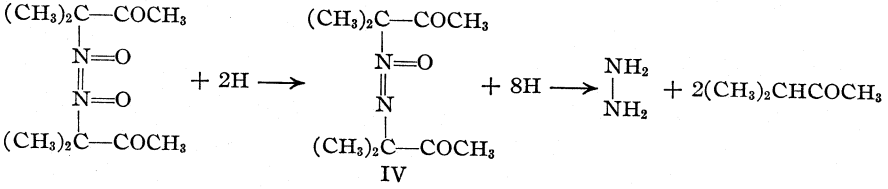
[4] Victor Meyer, *Ber.*, **21**, 1293 (1888).

The compounds were insoluble in alkali whereas isonitroso ketones (oximes) dissolve with a yellow color. It is extremely unlikely that this true nitroso group is elsewhere than on the only tertiary carbon atom, namely, the $\alpha$-carbon atom of the isopropyl group.

Faworski has shown that when ketones of the type $(CH_3)_2CHCOCH_2R$ are treated with phosphorus pentabromide substitution of the first bromine atom takes place entirely on the $\alpha$-carbon atom of the isopropyl group.[5] Oxidation of such ketones cleaves the ketone for the most part on the isopropyl side.[6]

It is perhaps surprising, therefore, that nitrosation occurs on the $\alpha$-carbon of the ethyl group to such a large extent when ethyl isopropyl ketone is treated with an equivalent quantity of ethyl nitrite. Experiments now under way indicate that other ketones of the same type manifest a similar behavior with nitrous acid. Our results are in keeping with those of Fileti and Ponzio, who find that ethyl isopropyl ketone upon oxidation with nitric acid yields acetylisobutyryl.

The reduction of bimolecular methyl $\alpha$-nitrosoisopropyl ketone by stannous chloride and hydrochloric acid yielded unexpected results. No detectable amount of methyl $\alpha$-aminoisopropyl ketone was formed. The final products were hydrazine and methyl isopropyl ketone. If the reduction were stopped after twenty minutes even in the presence of excess reducing agent, a water-insoluble crystalline intermediate could be isolated. This intermediate had the chemical composition and molecular weight of 2-azoxy-2-methyl-3-butanone (IV) (methyl $\alpha$-azoxyisopropyl ketone). Upon reduction with stannous chloride and hydrochloric acid it yielded hydrazine and methyl isopropyl ketone. We regard this as strong evidence that the compound contains the azoxy group, although this is not a characteristic reaction of aromatic azoxy compounds. The reduction of dimolecular methyl $\alpha$-nitrosoisopropyl ketone is thus formulated as follows




IV

The only aliphatic azoxy compound we have found in the literature is *sym.*-tetramethyldinitroazoxymethane,[7] obtained by the action of hydroxylamine on propylpseudonitrol. Upon reduction with zinc dust and acetic acid it yields acetoxime.[8]

[5] Faworski, *J. prakt. Chem.*, [2] **88**, 641 (1913).
[6] Wagner, *ibid.*, **44**, 280 (1891).
[7] Scholl and Born, *Ber.*, **28**, 1367 (1895).
[8] Schäfer, *ibid.*, **34**, 1914 (1901).

The reduction of bimolecular ethyl α-nitrosoisopropyl ketone did not give ethyl α-aminoisopropyl ketone but as yet no products have been isolated.

The peculiar behavior of these nitroso ketones on reduction led us to examine the literature for cases in which aliphatic true nitroso compounds had been reduced. Perhaps on account of the difficulty of preparation very little work has been done. The yields of reduction products are, as a rule, poor and it is hard to draw any general conclusions. However, *up to the present it has not been demonstrated that the main product of reduction of true aliphatic nitroso compounds as a class is the corresponding amine.*[9] We have not been able to find any case in which either an azoxy compound or the denitrogenated compound and hydrazine are the final products.

Experiments were carried out upon the reduction of α-nitrosoisopropyl acetone using in one case stannous chloride and hydrochloric acid and in another sodium amalgam and water. Here also no appreciable amounts of the expected amino ketone were obtained, the chief products being ammonia and non-nitrogenous substances. In both cases, however, it is quite likely that the nitroso compound is decomposed before reduction as demonstrated in the experimental section, and for this reason the experiments upon the reduction of this compound have been temporarily abandoned.

The work on nitroso compounds is being continued from two points of view. The comparative ease of nitrosation on the α-carbon atom of various alkyl groups of ketones is being investigated. The reduction of various types of nitroso compounds is being studied in detail and possible intermediates investigated.

## Experimental

**Bimolecular Methyl α-Nitrosoisopropyl Ketone.**—To 125 g. (1.45 moles) of methyl isopropyl ketone[10] in a flask fitted with a reflux condenser, was added 6.7 cc. of concentrated hydrochloric acid. The mixture was kept at 45–55° and the theoretical quantity of gaseous ethyl nitrite[11] was passed in over two hours. During the process the reaction

[9] In the following references are recorded cases in which true nitroso compounds of the aliphatic series have been reduced yielding the amine or hydroxyl amine in but small yields or only ammonia: Baeyer, *Ber.*, **28,** 2292 (1895); Cusmano, *Atti accad. Lincei*, **26,** II, 87 (1917) [*Chem. Abstracts*, **12,** 1183 (1918)]; Demjanow, *Chem. Zentr.*, I, 1064 (1899); *Ber.*, **40,** 245 (1907); Earl and Kenner, *J. Chem. Soc.*, 2142 (1927); Gomberg, *Ann.*, **300,** 79 (1898); Hantzsch, *Ber.*, **35,** 2979, 4120 (1902); Schmidt, *ibid.*, **35,** 2329, 3733, 3728 (1902); *ibid.*, **36,** 1766 (1903); Schmidt and Austin, *ibid.*, **36,** 1772 (1903); Schmidt and Leipprand, *ibid.*, **37,** 537, 546 (1904); Schmidt and Widmann, *ibid.*, **42,** 497, 1893 (1909); Schmidt and Dieterle, *Ann.*, **377,** 48 (1910); Tonnies, *Ber.*, **12,** 169 (1879).

[10] We wish to thank Dean F. C. Whitmore and his students for supplying us with large quantities of this ketone for which they have developed an excellent method of preparation soon to be published.

[11] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1930, Vol. X, p. 22.

mixture turned green. At the end of the process the reaction mixture was placed in the ice box for three hours when crystalline plates with pyramid faces were deposited. The mixture was finally chilled with freezing mixture. The crystals were filtered off and washed with ether; yield, 40 g. (0.17 mole), of almost pure bis-nitroso ketone (m. p. 99–101°) (24% of the theoretical). The product, after crystallization from chloroform and petroleum ether, melted at 101.5–102° with decomposition.

*Anal.* Calcd. for $(C_6H_9O_2N)_2$: C, 52.2; H, 7.88; mol. wt., 230. Found: C, 52.2; H, 7.92; mol. wt. (cryoscopic in benzene), 231.

The compound is soluble in chloroform, less so in benzene, and very slightly soluble in ether, and petroleum ether. It is insoluble in water. Upon heating solutions of this compound in benzene or chloroform they slowly become bluish green; upon cooling this color disappears. It is insoluble in dilute sodium hydroxide. This compound has previously been obtained by Cusmano from the corresponding isonitro amine.[12] He records the melting point as 99° and that its solutions are not colored blue. Upon evaporating the filtrate from the bis-nitroso compound *in vacuo* at 40° a further 2.5 g. was obtained and 14 g. of liquid residue. The latter was dissolved in 100 cc. of 10% aqueous sodium hydroxide. The solution after extraction with chloroform and ether was acidified and extracted with ether. The ether extract upon evaporation yielded 0.5 g. residue, which after washing with benzene was almost pure methylglyoxime, m. p. 147–150°. The same material was obtained in somewhat larger quantities (1.5 g.) when 0.7 mole of ketone was treated with 100% excess of ethyl nitrite. The yield of bis-nitroso ketone was thereby considerably reduced, being only 0.043 mole or 6% of the theoretical. The methylglyoxime obtained in this case after crystallization from ether and benzene melted 150–152°. The identity of both samples was established by a mixed melting point (150–152°) with a known sample of methylglyoxime m. p. 156°, and by analysis.[13]

*Anal.* Calcd. for $C_3H_6O_2N_2$: C, 35.3; H, 5.93; N, 27.5. Found: C, 36.1, 36.2; H, 6.03, 5.95; N (Dumas), 28.0.

The sample was evidently not quite pure as also indicated by its melting point but there was insufficient material to purify further the analytical sample.

**Bimolecular Ethyl α-Nitrosoisopropyl Ketone.**—Into 92 g. (0.92 mole) of ethyl isopropyl ketone and 5.3 cc. of concentrated hydrochloric acid was passed 0.92 mole of ethyl nitrite, as previously, keeping the temperature 30–40°. During the reaction the mixture turned green and white crystals of the bis-nitroso compound were deposited. At the end of the reaction the mixture was cooled and the crystals were filtered off; yield 8.0 g. (0.031 mole), of almost pure compound (6.8% of the theoretical); m. p. after recrystallization from alcohol, 119.2–120°.

*Anal.* Calcd. for $(C_6H_{11}O_2N)_2$: C, 55.7; H, 8.59; mol. wt., 258.2. Found: C, 55.8; H, 8.58; mol. wt. (cryoscopic in benzene), 241.

The compound is practically insoluble in hot or cold water, ether, cold alcohol and dilute sodium hydroxide solution but soluble in chloroform and hot alcohol. Upon heating its solutions they became blue but they became colorless again on cooling.

**α-Isonitrosoethyl Isopropyl Ketone.**—The liquid after filtering off the bis-nitroso compound, was neutralized with solid potassium carbonate, filtered, and distilled under reduced pressure from a bath at 34–36°. The residue on cooling yielded crystals of α-isonitrosoethyl isopropyl ketone. By distilling almost to dryness 32 g. (0.25 mole) of isonitroso compound was obtained; m. p. 92–93°, after recrystallization from chloroform and petroleum ether; yield 27% of the theoretical.

*Anal.* Calcd. for $C_6H_{11}O_2N$: C, 55.7; H, 8.59. Found: C, 55.4; H, 8.11.

[12] Cusmano, *Atti accad. Lincei*, **22**, I, 225–231; *Chem. Abstracts*, **7**, 2550 (1913).

[13] Charrier, *Gazz. chim. ital.*, **37**, II, 147 (1907); *Chem. Zentr.*, II, 1232 (1907).

The compound is soluble in chloroform, ether and alcohol and cold dilute sodium hydroxide solution but insoluble in petroleum ether and cold water. Solutions of the compound in sodium hydroxide were bright yellow; upon acidification the compound was precipitated and the solution became colorless. This latter behavior, along with the analysis and melting point, identified the compound as that obtained by Ponzio (m. p. 93–94°)[14] by the action of amyl nitrate on ethyl isopropyl ketone. This he proved to be isonitroso ethyl isopropyl ketone by the action of $N_2O_4$. The liquid distilled from the above reaction mixture in isolating the isonitroso compound was redistilled. It all distilled over between 77.3 and 78° and left only a slight residue. It was shown to contain ethyl isopropyl ketone by the isolation of the semicarbazone. By measurement of refractive index, it was estimated that it contained 16 g. of unreacted ketone (17%) which therefore probably forms a minimum boiling mixture with ethyl alcohol. Fifty per cent. of the original ketone has thus been accounted for; the remainder probably escaped isolation in the form of cleavage products.

**The Reduction of Bimolecular Methyl α-Nitrosoisopropyl Ketone.**—To a vigorously stirred solution of 84.5 g. (0.375 mole) of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 123 cc. of concentrated hydrochloric acid was added slowly 17.25 g. (0.15 mole) of finely ground bimolecular methyl α-nitrosoisopropyl ketone, keeping the temperature below 25° by running water. The mixture was then stirred at room temperature until all the insoluble material had gone into solution (five hours). The solution was then poured into 190 cc. of water and distilled until 150 cc. of distillate was collected, the first portion of which separated into two layers. This distillate after repeated fractionation and saturating the first fractions with potassium carbonate yielded a further quantity of the non-aqueous layer. In all, after drying with anhydrous potassium carbonate, 4.1 g. was obtained. This material upon fractional distillation yielded two fractions (1) 70–85°, 1.0 g., (2) 85–94°, 2.5 g. The last fraction was shown to be mostly methyl isopropyl ketone by converting into methyl isopropyl ketone semicarbazone which after recrystallization melted at 115–115.5°. A mixed melting point with a known sample established its identity.[15] The first fraction yielded a quantity of methyl isopropyl ketone semicarbazone which indicated that it also contained a considerable quantity of the ketone. The estimated yield of ketone is 0.036 mole, or 24% of the theoretical, assuming that 75% of the original 4.1 g. was methyl isopropyl ketone.

The acid residue from which the ketone was obtained was made strongly alkaline and distilled. The distillate was still coming over basic even after 1.5 liters had been distilled. The distillate was made acid with hydrochloric acid, evaporated to dryness on the steam-bath, and the resulting hydrochloride dried over calcium chloride and potassium hydroxide *in vacuo*. It weighed 1.7 g. and was shown to be hydrazine dihydrochloride by analysis and by treating with benzaldehyde to get dibenzal-azine whose identity was established by a mixed melting point with a known sample. There was no evidence that it contained appreciable quantities of any other base.

A better method of isolating the hydrazine dihydrochloride is to precipitate the tin from the residue with hydrogen sulfide after distilling out the ketone; evaporate almost to dryness, then add absolute alcohol, filter off the hydrochloride and wash with ether. In this way from 4.3 g. (0.037 mole) of the bis-nitroso compound, reduced as above, were obtained 0.79 g. (0.0075 mole) of almost pure hydrazine dihydrochloride; yield, 40% of the theoretical; 0.13 g. when treated with benzaldehyde gave 0.15 g. of dibenzal azine, m. p. 94–94.5° (after recrystallization).

**2-Azoxy-2-methyl-3-butanone (Methyl α-Azoxy Isopropyl Ketone).**—To a vigo-

[14] Ponzio, *Gazz. chim. ital.*, **27**, [1] 271–279 (1897).

[15] Faworski, *J. prakt. chem.*, [2] **88**, 684 (1913), gives m. p. 114° for methyl isopropyl ketone semicarbazone.

rously stirred solution of 84.5 g. (0.375 mole) of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 123 cc. of concentrated hydrochloric acid, 17.25 g. (0.15 mole) of bimolecular methyl α-nitroso isopropyl ketone was added over ten minutes, keeping the temperature at 18–21°. The bis-nitroso compound went into solution until about one-third had been added, then an insoluble material was observed to separate. When all the bis-nitroso compound had been added the reaction mixture was stirred for ten minutes and then poured into 500 cc. of cold water. The solution was immediately filtered. After washing the insoluble material with water and drying, it melted at 58.5–60°; yield, 10.0 g. (0.047 mole), (62% of theoretical).

It was recrystallized from ether and then from water and alcohol; flat prisms m. p. 60–61°.

Successive crystallizations from various solvents did not raise this melting point.

*Anal.* Calcd. for $C_{10}H_{18}O_3N_2$: C, 56.0; H, 8.47; N, 13.1; mol. wt. 214.2. Found: C, 55.8, 55.7, 56.4; H, 8.27, 8.35, 8.51; N, 13.6, 13.6; mol. wt. (cryoscopic in benzene), 215. (Between the second and third carbon and hydrogen analyses the compound was again recrystallized.)

The compound is soluble in methyl and ethyl alcohols, benzene, ether, chloroform, and carbon tetrachloride, but insoluble in water.

**Reduction of 2-Azoxy-2-methyl-3-butanone.**—Ten grams (0.047 mole) of the azoxy compound were stirred vigorously with 43.5 g. (0.193 mole) of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 63 cc. of concentrated hydrochloric acid until all had gone into solution (about fifteen hours). The reaction mixture was diluted with 100 cc. of water and the volatile non-basic substances distilled out. A second phase separated in the first fraction. By redistilling the distillate and saturating the first distillates with potassium carbonate, 4 g. of nonaqueous layer was obtained after drying with potassium carbonate. This liquid upon distillation gave two fractions: (1) 68–84°, 1.3 g.; (2) 84–94°, 1.1 g., the loss being due to manipulation. Fraction (2) was mostly methyl isopropyl ketone. This was shown by converting into methyl isopropyl ketone semicarbazone (m. p. 115–116.5°), which was identified by a mixed melting point. Fraction (1) upon treating with semicarbazide and sodium acetate yielded two semicarbazones. (A) That which first separated: 0.3 g., m. p. 115–116°, after recrystallization from alcohol and water; this was shown to be crude methyl isopropyl ketone semicarbazone by a mixed melting point with a known sample. (B) That which separated upon allowing the mother liquor from (A) to stand: 0.23 g. of solid m. p. 184–187° after recrystallization from hot water. This was shown to be acetone semicarbazone by a mixed melting point with a known sample (m. p. 188–189.5°).

On the assumption that 75% of the original 4 g. was methyl isopropyl ketone the yield is 0.035 mole or 37% of the theoretical.

One-half of the acid residue from the distillation was treated with hydrogen sulfide to precipitate the tin and evaporated. The residue was treated with absolute alcohol and the hydrochloride filtered off and dried. It was shown to be almost pure hydrazene dihydrochloride by analysis and conversion into dibenzalazine (m. p. 93–94°) which was identified by a mixed melting point. There was no evidence of an appreciable quantity of any other basic substances; yield, 0.9 g.; that is, 1.8 g. (0.017 mole) from 0.047 mole of azoxy (36.5% of the theoretical).

**Reduction of Bimolecular Ethyl α-Nitrosoisopropyl Ketone.**—The bis-nitroso compound was treated with stannous chloride and hydrochloric acid in the manner described for reducing bimolecular methyl α-nitrosoisopropyl ketone to the azoxy compound. From 4 g. was obtained 0.8 g. of an oil which upon combustion yielded an inorganic residue. No appreciable quantities of ethyl isopropyl ketone were found. The aqueous solution from the reduction was freed from tin by hydrogen sulfide and evapo-

rated. A negligible quantity of solid was left. Thus no basic substances were obtained although it was shown that all the nitroso compound had reacted. Further experiments upon the reduction of this nitroso compound will be carried out when larger quantities are available.

**The Reduction of Bimolecular 2-Nitroso-2-methyl-4-pentanone.**—The nitroso ketone was prepared by the oxidation of an aqueous solution of crude 2-hydroxylamino-2-methyl-4-pentanone oxalate with excess freshly precipitated mercuric oxide with mechanical stirring, keeping the temperature at 64–67°. The nitroso ketone was steam distilled from the reaction mixture under reduced pressure (150–210 mm.). The blue oil first coming over solidified to crystals of m. p. 72–74°. Recrystallization from chloroform did not raise the melting point; yield, 30%. Thus we could obtain this nitroso compound pure from the crude oxalate in one operation. Harries and Joblonski[16] prepared this compound by oxidation of the free hydroxylamine in boiling chloroform solution with yellow mercuric oxide. He reports a 60% yield of material, m. p. 75–76°. We believe that, in spite of the lesser yields, the fact that the starting product is the crude oxalate (obtained in 66% yields from mesityl oxide) makes our method more satisfactory because the preparation of the free hydroxylamine involves considerable trouble and loss.

The bis-nitroso compound, when reduced by stannous chloride and hydrochloric acid by the method already described in the case of bimolecular methyl α-nitrosoisopropyl ketone, yielded only mesityl oxide in 27% yield (identified by mixed melting point of its semicarbazone and refractive index), and ammonium chloride. The latter was isolated in 55% yield by first distilling out the mesityl oxide and precipitating the tin with hydrogen sulfide and then evaporating to dryness. It was identified by its chlorine analysis and behavior with alkali. It contained no appreciable quantities of hydrazine dihydrochloride as shown by its action with benzaldehyde.

The nitroso compound, however, upon stirring with concentrated hydrochloric acid at 10–11° went completely into solution with evolution of gas. Mesityl oxide was recovered from the solution in 55% yield by distillation. The fate of the nitroso group was not determined. The above results may thus have been due to preliminary cleavage by the hydrochloric acid.

Twenty grams nitroso compound were also reduced by shaking it with excess 2.5% sodium amalgam and water. The chief product was a non-nitrogen containing liquid of b. p. 217–219° (8.4 g. from 20 g. of nitroso compound). This substance was evidently a mixture as shown by analysis (C, 77.9, 78.0; H, 11.25, 11.03). On treating with sodium acetate and semicarbazide hydrochloride it gave a semicarbazone, m. p. 111–112°, in small yield. It was surprising to find that only a small quantity of basic material could be isolated. There were certainly none of the expected amines or hydrazine formed in the reduction.

## Summary

1. Bimolecular methyl α-nitrosoisopropyl and bimolecular ethyl α-nitrosoisopropyl ketone have been prepared by the action of ethyl nitrite on the corresponding ketones.

2. Bimolecular methyl α-nitrosoisopropyl ketone yields 2-azoxy-2-methyl-3-butanone upon reduction with stannous chloride and hydrochloric acid and the latter compound in turn is further reduced to methyl isopropyl ketone and hydrazine.

3. The reduction of α-nitrosoisopropyl acetone by stannous chloride

[16] Harries and Joblonski, *Ber.*, **31**, 1379 (1898).

and hydrochloric acid or by sodium amalgam and water gave neither the corresponding amine or hydrazine.

4. It is pointed out that there is no evidence that, as a rule, the true nitroso group in aliphatic compounds is reduced to the corresponding amine or hydroxylamine except in small yields.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

# THE NUMBER OF STEREOISOMERIC AND NON-STEREOISOMERIC PARAFFIN HYDROCARBONS

BY CHARLES M. BLAIR WITH HENRY R. HENZE

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No detailed attempt to relate the number of stereoisomeric and non-stereoisomeric paraffin hydrocarbons to their respective carbon contents is recorded in the chemical literature. Having first developed a mathematical relationship between carbon content and the number of structural isomers, both among the paraffin hydrocarbons[1] and their mono-substitution products,[2] the authors were successful in developing a series of recursion (finite) type formulas permitting the calculation of the number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins[3] from their carbon content. By utilizing a combination of the methods previously developed it is possible to derive analogous mathematical formulas by means of which the number of stereoisomeric and non-stereoisomeric paraffin hydrocarbons may be estimated accurately.

In this treatment we find it desirable to separate the paraffin hydrocarbons into classes according to whether their carbon content is even or odd. Those whose carbon content, $N$, is an even number are further divided into two groups: A, consisting of those isomeric hydrocarbons whose graphic formula may be divided into two parts of $N/2$ carbon atoms each; and B, the remaining hydrocarbons whose graphic formula cannot be so divided. Division of the graphic formula into two parts signifies breaking the single bond between two adjacent carbon atoms thus obtaining two alkyl radicals.

Likewise, the hydrocarbons whose carbon content, $N$, is an odd number are also divided into two groups: A, consisting of those isomers whose graphic formula can be divided into two parts, one of $(N + 1)/2$ carbon atoms and the other of $(N - 1)/2$ carbon atoms; and B, consisting of the remaining hydrocarbons whose graphic formula cannot be so divided.

**Group A. Even Carbon Content.**—If two alkyl radicals of $N/2$ carbon atoms each are combined, a hydrocarbon of $N$ carbon atoms is obtained,

[1] H. R. Henze and C. M. Blair, THIS JOURNAL, **53**, 3077–3085 (1931).

[2] H. R. Henze and C. M. Blair, *ibid.*, **53**, 3042–3046 (1931).

[3] C. M. Blair with H. R. Henze, *ibid.*, **54**, 1098 (1932).

and the number of stereoisomeric and non-stereoisomeric hydrocarbons that may be thus formed will depend upon the number of stereoisomeric and non-stereoisomeric alkyl radicals of $N/2$ carbon atoms. If the non-stereoisomeric alkyl radicals of $N/2$ carbon atoms are combined with themselves, no stereoisomers are formed, for no asymmetric carbon atoms are present in the radicals and none are created by the combination. However, when the non-stereoisomeric alkyl radicals of $N/2$ carbon atoms are combined with the stereoisomeric alkyl radicals of $N/2$ carbon atoms, one stereoisomer is formed with each possible combination and the number of such combinations will equal $As_{N/2} \cdot An_{N/2}$, where $As_{N/2}$ is the number of stereoisomeric alkyl radicals of $N/2$ carbon atoms, and $An_{N/2}$ is the number of non-stereoisomeric alkyl radicals of $N/2$ carbon atoms. Likewise, for the remaining type of combination of group A, in which the stereoisomeric alkyl radicals of $N/2$ carbon atoms are combined with themselves, one stereoisomer is formed with each possible combination and the number of these combinations will be $As_{N/2} \cdot (1 + As_{N/2})/2$. Hence, the total number of stereoisomers of group A, for even carbon content, will equal

$$As_{N/2} \cdot An_{N/2} + \frac{As_{N/2} \cdot (1 + As_{N/2})}{2}$$

The number of non-stereoisomers of group A, for even carbon content, is

$$\frac{An_{N/2} \cdot (1 + An_{N/2})}{2}$$

**Group A. Odd Carbon Content.**—In order to prevent duplication in determining the number of stereoisomers and non-stereoisomers in this group, it is necessary to recognize that part of the alkyl radicals of $(N + 1)/2$ carbon atoms may be derived from the alkyl radicals of $(N - 1)/2$ carbon atoms by the addition, to the free valence of the latter, of the —$CH_2$— group. Hence, the hydrocarbons resulting from combining such portions of the alkyls of $(N + 1)/2$ carbon atoms, that may be so derived, with the alkyls of $(N - 1)/2$ carbon atoms are considered as being formed by joining the alkyls of $(N - 1)/2$ carbon atoms to the alkyls of $(N - 1)/2$ carbon atoms through an intermediate carbon atom, and the number of stereoisomers so formed will equal $As_{(N-1)/2} \cdot An_{(N-1)/2} + As_{(N-1)/2} \cdot [1 + As_{(N-1)/2}]/2$. The number of non-stereoisomers formed in this way will equal $An_{(N-1)/2} \cdot [1 + An_{(N-1)/2}]/2$. The combination of the remaining stereoisomeric alkyl radicals of $(N + 1)/2$ carbon atoms with the radicals, both stereoisomeric and non-stereoisomeric, of $(N - 1)/2$ carbon atoms will form that number of stereoisomers represented by the expression $[As_{(N+1)/2} - As_{(N-1)/2}] \cdot T_{(N-1)/2}$ where $T_{(N-1)/2} = As_{(N-1)/2} + An_{(N-1)/2}$. The number of stereoisomers formed upon combination of the remaining non-stereoisomers of $(N + 1)/2$ carbon atoms with the stereoisomers of $(N - 1)/2$ carbon atoms, for combination with the non-stereoisomers of $(N - 1)/2$ carbon atoms would result in the forma-

tion of no stereoisomers, may be expressed as $[An_{(N+1)/2} - An_{(N-1)/2}] \cdot As_{(N-1)/2}$.

Therefore, the total number of stereoisomers in group A, for odd carbon content, will equal

$$\left[An\left(\frac{N+1}{2}\right) - An\left(\frac{N-1}{2}\right)\right] \cdot As\left(\frac{N-1}{2}\right) + T\left(\frac{N-1}{2}\right) \cdot As\left(\frac{N+1}{2}\right) - \frac{As\left(\frac{N-1}{2}\right) \cdot \left[As\left(\frac{N-1}{2}\right) - 1\right]}{2}$$

The number of non-stereoisomers in group A, for odd carbon content, will be

$$\left[An\left(\frac{N+1}{2}\right) - An\left(\frac{N-1}{2}\right)\right] \cdot An\left(\frac{N-1}{2}\right) + \frac{An\left(\frac{N-1}{2}\right) \cdot \left[1 + An\left(\frac{N-1}{2}\right)\right]}{2}$$

**Group B.**—If the graphic formula of a hydrocarbon of even carbon content cannot be divided into two parts of $N/2$ carbon atoms each, there must be in the formula one carbon atom, and only one, to which are attached branches none of which may contain more than $(N/2 - 1)$ carbon atoms. Obviously, there must be at least three branches and, since carbon has only four valences, there cannot be more than four branches.

Similarly, for those hydrocarbons of odd carbon content whose graphic formulas cannot be divided into two parts, one of $(N + 1)/2$ carbon atoms and the other of $(N - 1)/2$ carbon atoms, there must be in each of such formulas one carbon atom, and only one, to which are attached branches none of which may contain more than $(N - 3)/2$ carbon atoms. By a treatment similar to that already utilized in the case of the hydrocarbons of even carbon content, it may be shown that this specified carbon atom must have attached to it either three or four branches.

Hence, the isomeric hydrocarbons of group B, both even and odd, will be of two types: (a) those in which three branches are attached to the specified carbon atom; and (b) those in which four are attached to the specified carbon atom. The total number of stereoisomers and non-stereoisomers of group B will be obtained by a summation of the numbers in types (a) and (b).

Type (a) would seem to consist of three possible cases: (1) in which all three branches were of different carbon content; (2) in which two of the branches were of the same carbon content and different from that of the third; (3) in which all three branches were of the same carbon content. All three of these cases are actually possible but all will not necessarily be present with every value of $N$. The number of stereoisomers and non-stereoisomers in each case may be calculated by the following mathematical formula of the (finite) recursion type for that particular case.[4]

[4] The derivations of these formulas are exactly analogous to those for similar cases of the tertiary mono-substitution products of the paraffins which have been described by the authors. THIS JOURNAL, **54**, 1098 (1932).

Case (1)

Stereoisomers

$$2\Sigma T_i \cdot T_j \cdot T_k \qquad (sa_1)$$

Non-stereoisomers

$$\text{None} \qquad (na_1)$$

where $i + j + k = N - 1$; $i, j$ and $k$ are integers, distinct, and greater than zero; $i > j > k$; $i$, for even carbon content, is never greater than $(N/2 - 1)$; $i$, for odd carbon content, is never greater than $(N - 3)/2$.

Case (2)

Stereoisomers

$$\Sigma\{[(T_i)^2 - An_i] \cdot T_j + An_i \cdot As_j\} \qquad (sa_2)$$

Non-stereoisomers

$$\Sigma An_i \cdot An_j \qquad (na_2)$$

where $2i + j = N - i$ and $j$ are integers, distinct, and greater than zero; for even carbon content, neither $i$ nor $j$ may be greater than $(N/2 - 1)$; for odd carbon content, neither $i$ nor $j$ may be greater than $(N - 3)/2$.

Case (3)

Stereoisomers

$$\frac{2T_i + (T_i)^3}{3} - (An_i)^2 \qquad (sa_3)$$

Non-stereoisomers

$$(An_i)^2 \qquad (na_3)$$

where $3i = N - 1$; and $i$ is an integer greater than zero.

Type (b) would seem to consist of five possible cases: (1) in which all four branches are of different carbon content; (2) in which two of the branches are of the same carbon content and each of the others of different content; (3) in which three branches are of the same carbon content and different from that of the fourth; (4) in which all four branches are of the same carbon content; and (5) in which the four branches can be divided into two sets of two branches each, the individual members of each set being of the same carbon content but differing in content from the members of the other set. It will be seen that cases (4) and (5), though theoretically possible for hydrocarbons of both even and odd carbon content, are actually possible only for the latter, since in case (4) $(N - 1)$ must be divisible by four, and in case (5) $(N - 1)$ must be divisible by two. The number of stereoisomers and non-stereoisomers in each case may be calculated by the following mathematical formula of the (finite) recursion type for that particular case.

Case (1)

Stereoisomers

$$2\Sigma T_h \cdot T_i \cdot T_j \cdot T_k \qquad (sb_1)$$

Non-stereoisomers

$$\text{None} \qquad (nb_1)$$

where $h + i + j + k = N - 1$; $h, i, j$ and $k$ are integers, distinct, and greater than zero; $h > i > j > k$; $h$, for even carbon content, is never greater

than $(N/2 - 1)$; $h$, for odd carbon content, is never greater than $(N - 3)/2$.

Case (2)

Stereoisomers

$$\Sigma\{[(T_i)^2 - An_i]\cdot T_j\cdot T_k + An_i\cdot As_j\cdot T_k + An_i\cdot An_j\cdot As_k\} \qquad (sb_2)$$

Non-stereoisomers

$$\Sigma An_i\cdot An_j\cdot An_k \qquad (nb_2)$$

where $2i + j + k = N - 1$; and $i$, $j$ and $k$ are integers, distinct, and greater than zero.

Case (3)

Stereoisomers

$$\Sigma\left\{\left[\frac{2T_i + (T_i)^3}{3} - (An_i)^2\right]\cdot T_j + (An_i)^2\cdot As_j\right\} \qquad (sb_3)$$

Non-stereoisomers

$$(An_i)^2\cdot An_j \qquad (nb_3)$$

where $3i + j = N - 1$; and $i$ and $j$ are integers, distinct, and greater than zero.

Case (4)

Stereoisomers

$$\frac{(T_i)^4 + 11(T_i)^2 - 6An_i\cdot[1 + (An_i)^2]}{12} \qquad (sb_4)$$

Non-stereoisomers

$$\frac{An_i\cdot[1 + (An_i)^2]}{2} \qquad (nb_4)$$

where $4i = N - 1$; and $i$ is an integer greater than zero.

Case (5)

Stereoisomers

$$\tfrac{1}{2}\Sigma[(T_i\cdot T_j)^2 + T_i\cdot T_j - An_i\cdot An_j\cdot(An_i + An_j)] \qquad (sb_5)$$

Non-stereoisomers

$$\frac{An_i\cdot An_i\cdot(An_i + An_j)}{2} \qquad (nb_5)$$

where $2i + 2j = N - 1$; $i$ and $j$ are integers, distinct, and greater than zero; and $i > j$.

The total number of stereoisomeric and non-stereoisomeric hydrocarbons of $N$ carbon atoms may be determined by adding to the number of stereoisomers and non-stereoisomers calculated in group A the summation of the number calculated in each of the cases of group B.

The actual meaning and use of these recursion type formulas[5] may be illustrated in the calculation of the number of stereoisomeric and non-stereoisomeric tetradecanes.

[5] In using these recursion formulas to calculate the total number of isomeric paraffins of any specified carbon content it is necessary to make a preliminary calculation of the total number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins of $N/2$ and lesser carbon contents. The totals for such isomers through $C_{20}$ are recorded in Table I, THIS JOURNAL, **54**, 1105 (1932).

## Sample Calculation[6]

Group A. $N = 14$; $N/2 = 7$

Stereoisomers

$$As_7 \cdot An_7 + As_7(1 + As_7)/2 = 60.14 + 60(1 + 60)/2 = 2670$$

Non-stereoisomers

$$An_7(1 + An_7)/2 = 14(1 + 14)/2 = 105$$

Group B. $N - 1 = 13$; $N/2 - 1 = 6$

Type (a)

Case (1)

Stereoisomers

$$2 \cdot T_6 \cdot T_5 \cdot T_2 = 2 \cdot 28 \cdot 11 \cdot 1 = 616$$
$$2 \cdot T_6 \cdot T_4 \cdot T_3 = 2 \cdot 28 \cdot 5 \cdot 2 = 560$$

Non-stereoisomers

There can be no non-stereoisomers of this type

Case (2)

Stereoisomers

$$(T_6^2 - An_6)T_1 + An_6 \cdot As_1 = (28^2 - 8)1 + 8 \cdot 0 = 776$$
$$(T_5^2 - An_5)T_3 + An_5 \cdot As_3 = (11^2 - 5)2 + 5 \cdot 0 = 232$$
$$(T_4^2 - An_4)T_5 + An_4 \cdot As_5 = (5^2 - 3)11 + 3 \cdot 6 = 260$$

Non-stereoisomers

$$An_6 \cdot An_1 = 8 \cdot 1 = 8$$
$$An_5 \cdot An_3 = 5 \cdot 2 = 10$$
$$An_4 \cdot An_5 = 3 \cdot 5 = 15$$

Case (3)

This case is not actually possible for this carbon content

Type (b)

Case (1)

Stereoisomers

$$2 \cdot T_6 \cdot T_4 \cdot T_2 \cdot T_1 = 2 \cdot 28 \cdot 5 \cdot 1 \cdot 1 = 280$$
$$2 \cdot T_5 \cdot T_4 \cdot T_3 \cdot T_1 = 2 \cdot 11 \cdot 5 \cdot 2 \cdot 1 = 220$$

Non-stereoisomers

There can be no non-stereoisomers of this type

Case (2)

Stereoisomers

$$(T_5^2 - An_5)T_2 \cdot T_1 + An_5 \cdot As_2 \cdot T_1 + An_5 \cdot An_2 \cdot As_1 = (11^2 - 5)1 \cdot 1 + 5 \cdot 0 \cdot 1 + 5 \cdot 1 \cdot 0 = 116$$
$$(T_4^2 - An_4)T_3 \cdot T_2 + An_4 \cdot As_3 \cdot T_2 + An_4 \cdot An_3 \cdot As_2 = (5^2 - 3)2 \cdot 1 + 3 \cdot 0 \cdot 1 + 3 \cdot 2 \cdot 0 = 44$$
$$(T_3^2 - An_3)T_6 \cdot T_1 + An_3 \cdot As_6 \cdot T_1 + An_3 \cdot An_6 \cdot As_1 = (2^2 - 2)28 \cdot 1 + 2 \cdot 20 \cdot 1 + 2 \cdot 8 \cdot 0 = 96$$
$$(T_3^2 - An_3)T_5 \cdot T_2 + An_3 \cdot As_5 \cdot T_2 + An_3 \cdot An_5 \cdot As_2 = (2^2 - 2)11 \cdot 1 + 2 \cdot 6 \cdot 1 + 2 \cdot 5 \cdot 0 = 34$$
$$(T_2^2 - An_2)T_6 \cdot T_3 + An_2 \cdot As_6 \cdot T_3 + An_2 \cdot An_6 \cdot As_3 = (1^2 - 1)28 \cdot 2 + 1 \cdot 20 \cdot 2 + 1 \cdot 8 \cdot 0 = 40$$
$$(T_2^2 - An_2)T_5 \cdot T_4 + An_2 \cdot As_5 \cdot T_4 + An_2 \cdot An_5 \cdot As_4 = (1^2 - 1)11 \cdot 5 + 1 \cdot 6 \cdot 5 + 1 \cdot 5 \cdot 2 = 40$$
$$(T_1^2 - An_1)T_6 \cdot T_5 + An_1 \cdot As_6 \cdot T_5 + An_1 \cdot An_6 \cdot As_5 = (1^2 - 1)28 \cdot 11 + 1 \cdot 20 \cdot 11 + 1 \cdot 8 \cdot 6 = 268$$

[6] The number of terms actually present in all theoretically possible cases of types (a) and (b) through $C_{40}H_{82}$ are recorded in Table I, THIS JOURNAL, **53**, 3084 (1931).

Non-stereoisomers

$$An_5 \cdot An_2 \cdot An_1 = 5 \cdot 1 \cdot 1 = 5$$
$$An_4 \cdot An_3 \cdot An_2 = 3 \cdot 2 \cdot 1 = 6$$
$$An_3 \cdot An_6 \cdot An_1 = 2 \cdot 8 \cdot 1 = 16$$
$$An_3 \cdot An_5 \cdot An_2 = 2 \cdot 5 \cdot 1 = 10$$
$$An_2 \cdot An_6 \cdot An_3 = 1 \cdot 8 \cdot 2 = 16$$
$$An_2 \cdot An_5 \cdot An_4 = 1 \cdot 5 \cdot 3 = 15$$
$$An_1 \cdot An_6 \cdot An_5 = 1 \cdot 8 \cdot 5 = 40$$

Case (3)

Stereoisomers

$$[(2 \cdot T_4 + T_4^3)/3 - T_4^2]T_1 + An_4^2 \cdot As_1 = [(2 \cdot 5 + 5^3)/3 - 3^2] \cdot 1 + 3^2 \cdot 0 = 36$$
$$[(2 \cdot T_3 + T_3^3)/3 - T_3^2]T_4 + An_3^2 \cdot As_4 = [(2 \cdot 2 + 2^3)/3 - 2^2] \cdot 5 + 2^2 \cdot 2 = 8$$

Non-stereoisomers

$$An_4^2 \cdot An_1 = 3^2 \cdot 1 = 9$$
$$An_3^2 \cdot An_4 = 2^2 \cdot 3 = 12$$

Thus, of the tetradecanes there are 6296 stereoisomers and 267 non-stereoisomers.

The number of stereoisomeric and non-stereoisomeric paraffins, as calculated by the use of these recursion type formulas, through the eicosanes is shown in Table I. It should be noted that these formulas were derived solely by adaptation of the theoretical considerations utilized in the three previous contributions of this series. Having made the calculations recorded in Table I, the respective totals of the series $CH_4$ to $C_{14}H_{30}$ were checked by actually writing the various structural formulas and counting the number of stereoisomers and non-stereoisomers occasioned by the presence of asymmetric and pseudo-asymmetric carbon atoms. The numbers so obtained agreed exactly with those predicted by the above calculations.

TABLE I

NUMBER OF STEREOISOMERIC AND NON-STEREOISOMERIC PARAFFIN HYDROCARBONS

| Carbon content | Stereo-isomers | Non-stereo-isomers | Total | Carbon content | Stereo-isomers | Non-stereo-isomers | Total |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 1 | 1 | 11 | 290 | 55 | 345 |
| 2 | 0 | 1 | 1 | 12 | 804 | 96 | 900 |
| 3 | 0 | 1 | 1 | 13 | 2,256 | 156 | 2,412 |
| 4 | 0 | 2 | 2 | 14 | 6,296 | 267 | 6,563 |
| 5 | 0 | 3 | 3 | 15 | 17,689 | 433 | 18,122 |
| 6 | 0 | 5 | 5 | 16 | 49,952 | 747 | 50,699 |
| 7 | 4 | 7 | 11 | 17 | 142,016 | 1,239 | 143,255 |
| 8 | 11 | 13 | 24 | 18 | 406,330 | 2,089 | 408,419 |
| 9 | 35 | 20 | 55 | 19 | 1,169,356 | 3,498 | 1,172,854 |
| 10 | 101 | 35 | 136 | 20 | 3,390,052 | 5,912 | 3,395,964 |

## Summary

1. By means of a separation of the isomeric hydrocarbons of each specified carbon content into types, arbitrarily chosen upon the basis of

their structural formulas, a relationship may be established between the number of stereoisomeric and non-stereoisomeric paraffins and the alkyl groups of which the former may be considered to be composed. Mathematical formulas of the recursion (finite) type are advanced which permit of the calculation, from their carbon content, of the number of stereoisomeric and non-stereoisomeric paraffins in each of these structural types. In using these recursion formulas to calculate the total of such isomers of any specified carbon content, the total number of stereoisomeric and non-stereoisomeric alkyl groups of $N/2$ and all lesser carbon contents must be known.

2. The total number of isomers so obtained agrees exactly through the tetradecanes with the numbers required by theory as tested by actually writing the structural formulas and counting the number of stereoisomers and non-stereoisomers.

AUSTIN, TEXAS

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[CONTRIBUTION NO. 85 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

## PREPARATION OF 1,2,3,4-TETRABROMOBUTANE

BY RALPH A. JACOBSON

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One of the methods described in the literature for the laboratory preparation of 1,3-butadiene is that of Harries,[1] in which 2,3-dibromobutane is decomposed by soda lime at 600°. Although this method does not yield pure butadiene, the latter can be obtained by converting the impure product into 1,2,3,4-tetrabromobutane, and then reducing this compound with zinc and alcohol according to the method of Thiele.[2] The tetrabromo compound therefore represents a convenient source of pure butadiene. In connection with a problem requiring rather large amounts of butadiene, a modification of Harries' method was employed as a preparative procedure for 1,2,3,4-tetrabromobutane. As a result, considerable data were collected and several changes in the apparatus and procedure were made which render the method somewhat more reliable and convenient.[3]

The original Harries method involved dropping 2,3-dibromobutane upon soda-lime contained in an iron pot at 600°. The butadiene and

[1] Harries, *Ann.*, **383**, 176 and 181 (1911).

[2] Thiele, *ibid.*, **308**, 333 (1899); Birch, *Ind. Eng. Chem.*, **20**, 474 (1928); Farmer, Lawrence and Thorpe, *J. Chem. Soc.*, 729 (1928).

[3] Recently Muskat and Northrup [THIS JOURNAL, **52**, 4050 (1930)], have described a laboratory method of preparing butadiene which involves the following operations: (1) converting butyl alcohol into butyl chloride, (2) chlorinating butyl chloride to dichlorobutane and (3) converting dichlorobutane into butadiene by passing it over heated soda-lime.

other gaseous products were passed through an ice condenser, after which the butadiene was absorbed in bromine yielding 1,2,3,4-tetrabromobutane. In place of the iron pot, a pipe furnace similar to that used by Adams, Kamm and Marvel[4] for the preparation of amylene proved to be more convenient. Also, less charring occurred and somewhat better yields were obtained by carrying out the reaction at 530–550° instead of at 600°. Saturation of the soda-lime with carbon dioxide, as recommended by Harries, was found to be unnecessary since no improvement in the yield resulted. Purification of the crude 1,2,3,4-tetrabromobutane was effected by crystallization from alcohol. Among the by-products isolated in small amounts were *trans*-2-bromo-2-butene, 1,2-dibromobutane, 2,3-dibromobutane, 1,3-dibromobutane, 1,4-dibromobutane, isomeric 1,2,3,4-tetrabromobutane and 1,1,4,4-tetrabromobutane.

In two of the experiments, crotyl chloride[5] was employed instead of 2,3-dibromobutane. The reaction between crotyl chloride and soda lime occurred at lower temperatures and with less charring than in the case of 2,3-dibromobutane. Since, also, both the theoretical and actual yields of 1,2,3,4-tetrabromobutane were in excess of those obtained with 2,3-dibromobutane, the use of crotyl chloride is to be recommended. While the yield of 1,2,3,4-tetrabromobutane from either 2,3-dibromobutane or crotyl chloride is not entirely satisfactory, the apparatus required is simple and the procedure can be carried out by a non-technical laboratory assistant.

## Experimental

**Apparatus.**—The apparatus consisted of a horizontal iron pipe 5 cm. in diameter and 152 cm. in length, wound with 13.7 meters of number 18 nichrome wire, imbedded in alundum cement, and covered with magnesia. Near one end a vertical section of pipe 2.5 × 20 cm. was welded to the furnace. This end was closed by a screw cap to which was welded a 13-mm. thermocouple well extending inward to the center of the furnace. The other end was fitted with a screw cap to which was attached a section of iron pipe 2.5 × 20 cm. The furnace was connected to a train consisting of two vertical Liebig ice condensers attached to 1-liter flasks (A) and (B) packed in ice, two gas-washing bottles (C) and (D) containing bromine also surrounded by ice, and a trap (E) packed in carbon dioxide snow.

**Procedure.**—The furnace was used on a 220 d.c. line with suitable resistance in the circuit for regulating the temperature. Preliminary runs had shown that at temperatures of 600° and above large amounts of tarry products were formed. In a typical run the furnace was packed with 914 g. of soda lime and heated to 530–550°. By means of a separatory funnel inserted in the vertical section of pipe, 600 g. of 2,3-dibromobutane was dropped into the furnace at such a rate that the escaping gas passed into the bromine rapidly but not violently. A slight pressure of nitrogen was maintained on the liquid in the separatory funnel to avoid the escape of gas bubbles through the liquid.

[4] Adams, Kamm and Marvel, "University of Illinois Bulletin," **16**, No. 43, 13 (1919).

[5] Charon [*Ann. chim. phys.* [7] **17**, 234 (1899)], prepared 1,3-butadiene by heating crotyl bromide and potassium formate in a sealed tube.

Approximately two hours were required for the addition of the bromide and an additional half hour for sweeping out the apparatus with a slow stream of nitrogen. When the run was completed, the excess bromine was distilled from the crystals of 1,2,3,4-tetrabromobutane, the latter filtered from the small amount of accompanying products, and washed with alcohol. Crystallization of the product from alcohol gave white plates or needles melting at approximately 112°. A second crystallization from alcohol gave the pure product melting at 116–117°. The yield of pure 1,2,3,4-tetrabromobutane per 600-g. run varied from 140 to 150 g. (13.5 to 14.5% of the theoretical). In two experiments with crotyl chloride, the yields at 550° and at 400° were, respectively, 16.4 and 19.3% of the theoretical.

**Examination of Condensates (A) and (B).**—The condensates (A) and (B) from eleven runs with 2,3-dibromobutane were combined and distilled. The gas liberated upon gentle warming of the mixture was absorbed in bromine and yielded 50 g. of 1,2,3,4-tetrabromobutane. Following the separation of 545 g. of water, fractional distillation of the residue yielded 45 g. of a liquid boiling at 90.5–92.5°, which from its boiling point and analysis appeared to be *trans*-2-bromo-2-butene. In addition, 50 g. of 2,3-dibromobutane, b. p. 157.5–159°, was collected as well as several intermediate fractions containing unsaturated compounds that were not purified and identified.

ANALYSES

| | Bromine calcd. | Bromine found | |
|---|---|---|---|
| *Trans*-2-bromo-2-butene | 59.24 | 59.07 | 58.89 |
| 2,3-Dibromobutane | 74.04 | 73.83 | 74.05 |

**Examination of By-products Accompanying 1,2,3,4-Tetrabromobutane.**—The liquid residues (790 g.) from six runs after filtration of the crude 1,2,3,4-tetrabromobutane were combined and distilled at atmospheric pressure. Separation into a volatile portion (345 g.) and a non-volatile portion (440 g.) was thereby effected. Fractional distillation of the volatile portion yielded 1,2-dibromobutane, 1,3-dibromobutane, 2,3-dibromobutane and 1,4-dibromobutane.

The non-volatile portion (300 g.) upon cooling in ice deposited crystals of 1,2,3,4-tetrabromobutane (106 g.). Fractional distillation under reduced pressure of the remaining liquid portion yielded 40 g. of 1,1,4,4-tetrabromobutane, and 42 g. of a tetrabromide which was probably the isomeric 1,2,3,4-tetrabromobutane. The table summarizes the by-products obtained.

TABLE I

SUMMARY OF BY-PRODUCTS OBTAINED

| Compound | B. p., °C. | B. p., "Int. Crit. Tables" | Yield, g. | Analyses, % Br calcd. | Br found | |
|---|---|---|---|---|---|---|
| 1,2-Dibromobutane | 165–166 | 166 | 59 | 74.04 | 74.09 | 74.23 |
| 2,3-Dibromobutane | 158–159 | 158 | 71 | 74.04 | 73.83 | 74.05 |
| 1,3-Dibromobutane | 173–175 | 174 | 15 | 74.04 | 74.14 | 74.20 |
| 1,4-Dibromobutane | 197–198 (dec.) | 198 (dec.) | 20 | 74.04 | 74.27 | 74.53 |
| 1,1,4,4-Tetrabromobutane | 133 (1 mm.) | 145 (10 mm.) | 40 | 85.55 | 85.55 | 85.57 |
| Isomeric 1,2,3,4-tetrabromobutane | M. p. 38 | M. p. 39 | 42 | 85.55 | 84.30 | 84.44 |

## Summary

1. Directions are given for the preparation of 1,2,3,4-tetrabromobutane from 2,3-dibromobutane and from crotyl chloride by passing these over

soda lime at elevated temperatures and subsequently absorbing the gaseous products in bromine.

2. The use of crotyl chloride for this purpose represents a more convenient procedure. Its use in preference to 2,3-dibromobutane is recommended because less charring occurs, the yields of 1,2,3,4-tetrabromobutane are better, and the temperature required for reaction is lower.

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

# THE SURFACE TENSION OF VARIOUS ALIPHATIC ACIDS PREVIOUSLY STUDIED FOR BACTERICIDAL ACTION TO MYCOBACTERIUM LEPRAE. XX[1]

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During a research on compounds possessing antileprocidal properties, a large number of aliphatic acids were prepared, many of which were found to be bactericidal *in vitro* toward *Mycobacterium leprae*. Since the effective acids differed from each other rather widely in chemical structure, it was concluded that their bactericidal effectiveness was due to a certain combination of physical properties common to all of these acids, rather than to any specific chemical structure as was at first thought probable. A study of the physical properties was undertaken to determine whether any correlation could be found between one or more of these and the bactericidal effectiveness of the acids.

During the bacteriological work the acids were usually tested for their effectiveness in the form of their soluble salts. It was noticed that, in general, the aqueous solutions of the sodium salts of the most effective acids were very soapy, whereas those of the ineffective acids were not. This suggested that the ability to form soapy solutions might be one of the important properties related to the bactericidal action of the acids, and hence that a correlation might exist between the bactericidal action and the surface tension of solutions of the acids in the form of their salts. A further indication of such a correlation was the fact that the acids were bactericidally effective *in vitro* only in a form in which the surface tension reducing action became effective, that is, in the form of the soluble salts. The free acids appeared to be effective only in so far as they were able to form soluble salts with the buffer of the media. The ethyl esters unable to form sodium salts were entirely ineffective *in vitro*.

[1] For the last papers in this field see Stanley, Jay and Adams, THIS JOURNAL, **51**, 1261 (1929); Ford and Adams, *ibid.*, **52**, 1259 (1930); Browning, Woodrow and Adams, *ibid.*, **52**, 1281 (1930); Armendt and Adams, *ibid.*, **52**, 1289 (1930); Greer and Adams, *ibid.*, **52**, 2540 (1930). In these and in previous papers the bactericidal action of these compounds may be found.

The relationship of surface tension depressants, usually the sodium salts of castor oil acids,[2] and bacteriological growth has been the subject of some study during recent years. It was found that in most cases lowering the surface tension of the media decreased the growth of the organism. Larson[3] found that all pellicle forming organisms ceased to grow at the surface when the surface tension of the medium was below 45 dynes per cm. Berczeller[4] has discussed the effect of surface tension on pharmacological action and Traube[5] and Somogyl believe that bacteriological activity is correlated with the surface tension of the medium. It therefore appeared quite probable that the bactericidal effectiveness of these aliphatic acids might be closely related to their surface tension depressant action.

In this investigation the surface tensions of aqueous and media solutions of the sodium salts of one hundred and twenty different aliphatic acids in several different dilutions have been determined. Acids having a cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl and one or more cyclohexyl groups, as well as hydroxy acids, unsaturated acids and certain naturally occurring acids such as hydnocarpic, chaulmoogric and ricinoleic acids were included among those tested. It was found that without exception all of the bactericidally effective aliphatic acids were marked surface tension depressants. However, while the surface tension depressant action is closely allied with the bactericidal action, it must not be regarded as the sole criterion of bactericidal effectiveness, for $\alpha$-bromopalmitic acid (Table VI), the total acids of cod liver oil and some of the acids having approximately nineteen or more carbon atoms were found to be good surface tension depressants and yet were relatively non-effective as bactericides. With the exception of these acids the surface tension paralleled the bactericidal effectiveness.

The present data indicate that a bactericidally effective acid must be a good surface tension depressant and must also have a molecular weight of approximately 256, that is, one which corresponds to an acid of sixteen carbon atoms. Decreasing the molecular weight of the acid below 256 caused a drop in bactericidal effectiveness and a parallel drop in surface tension effect while increasing the molecular weight above 256 caused a drop in bactericidal effectiveness usually without the corresponding drop in surface tension effect. Thus while one physical property, namely, surface tension depressant action, can be correlated directly with the bactericidal effectiveness of the acids, it is but one of two or more factors which are responsible for the bactericidal action of these aliphatic acids.

Several general qualitative correlations between chemical structure

[2] Wolf, *Biochem. J.*, **17**, 813 (1923).
[3] Larson, *J. Infectious Diseases*, **25**, 41 (1919).
[4] Berczeller, *Biochem. Z.*, **66**, 202 (1914).
[5] Traube, *ibid.*, **120**, 90 (1921).

and surface tension were revealed in this investigation. Regardless of the structure, the surface tension of solutions of the sodium salts of the acids, which is high for the low molecular weight acids, decreased with an increase in molecular weight and then began to increase slightly when the acid contained about nineteen carbon atoms (Fig. 1). A similar action was found in a normal fatty acid series of fourteen acids studied by Lascaray,[6] and of other similar acids studied by Dubrisay,[7] and by Walker.[8] The behavior of certain α-hydroxy fatty acids was just the reverse, an increase in molecular weight causing an increase in the surface tension (Table I, No. 8). A ring structure caused slight increase in surface tension over the

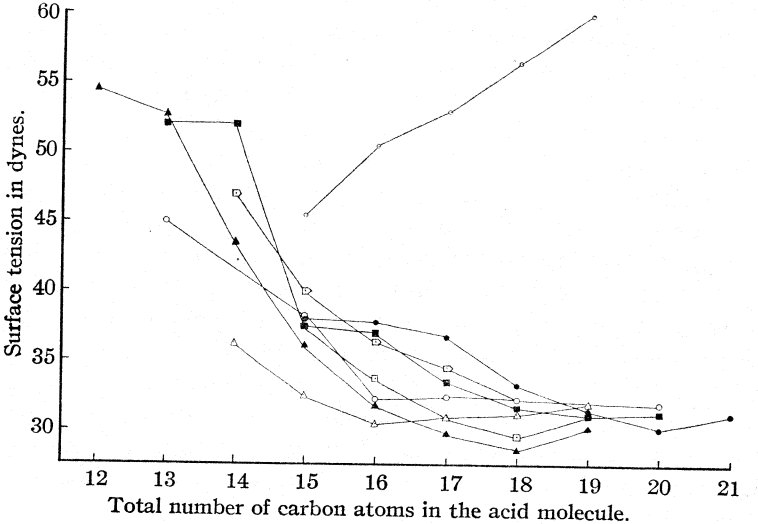


Fig. 1.—Change in surface tension with molecular weight: 1 : 500. ○, hydroxy acids; ○, allyl acids; ●, cyclopentenyl acids; △, cyclopropyl acids; □, cyclobutyl acids; ⊏>, cyclopentyl acids; ■, cyclohexyl acids; ▲, aliphatic (averaged).

corresponding straight-chained acids with the carboxyl group other than at the end of the chain (compare isomers in Table I, No. 1 to 4, Tables III and IV, with isomers in Table I, Nos. 9 to 17). The rather marked effect of a ring structure upon the properties of the acids with the carboxyl group at the end of the chain is especially to be noted (Table III). The introduction of an iso group caused a slight increase in the surface tension (Table I, Nos. 18 to 21, Tables II and V). The introduction of a double bond into the ring or carbon chain of the acids had no appreciable effect on the surface tension (compare Table I, Nos. 4 to 7 with Table I, No. 3 and Nos. 9 to 17). The

[6] Lascaray, *Kolloid Z.*, **34**, 73 (1924).
[7] Dubrisay, *Compt. rend.*, **178**, 1976 (1924).
[8] Walker, *J Chem. Soc.*, **119**, 1521 (1921).

concentration at which an acid had the minimum surface tension varied in an indefinite manner with the structure of the acid.

The position of the carboxyl group in the higher fatty acids is of especial interest. The sodium salts of palmitic and stearic acids formed a semi-solid gelatinous mass when present one part in 500 parts of water at 25°, whereas all the isomers with the carboxyl group at any other position than on the end carbon atom were quite soluble under the same conditions. The isomeric acids were even readily soluble in 10 to 20% solutions, forming perfectly fluid liquids. This great change in solubility

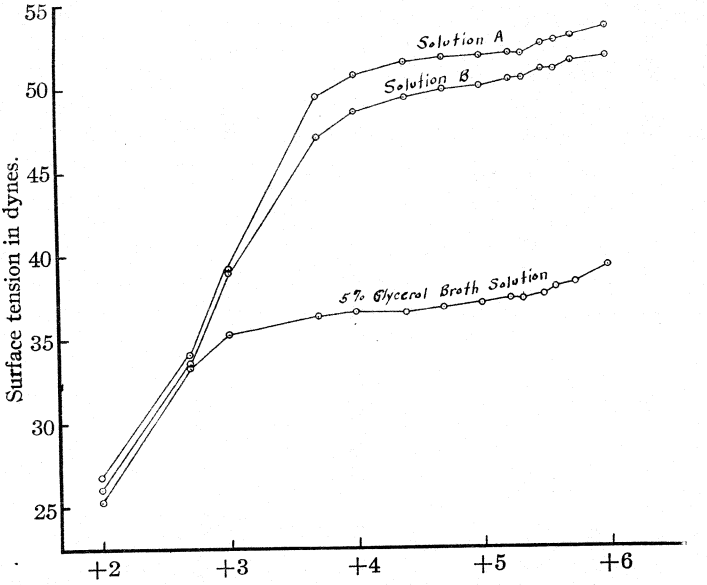


Fig. 2.—Changes of surface tension on dilution of sodium di-*n*-heptyl acetate: Tensiometer method.

caused by moving the carboxyl group from the end carbon atom to any other carbon atom, is especially interesting since palmitic and stearic acid have no bactericidal properties, while the isomers, especially of palmitic acid, possess a high bactericidal action. The shift of the carboxyl group to the second carbon atom caused a very large drop in the surface tension. The sodium salt of di-*n*-heptylacetic acid, an isomer of palmitic acid, the ethyl and glyceryl esters of which have been tested clinically, lowers the surface tension of water approximately 50 dynes per cm. in 0.1 molar solution and even 20 dynes per cm. in so dilute a solution as one part in one million parts of water (Fig. 2). As the carboxyl was moved farther down the chain, the surface tension increased slightly and then again de-

TABLE I

SURFACE TENSION IN DYNES PER CM. DILUTION, 1:500

| | R = | | $C_4H_9$ | $C_5H_{11}$ | $C_6H_{13}$ | $C_7H_{15}$ | $C_8H_{17}$ | $C_9H_{19}$ | $C_{10}H_{21}$ | $C_{11}H_{23}$ | $C_{12}H_{25}$ | $C_{13}H_{27}$ | $C_{14}H_{29}$ | $C_{15}H_{31}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Cyclopropylmethyl alkyl acetic acids $C_3H_5CH_2CH(COONa)R$ | T 25° | | 49.7 | | 45.1 | | 38.8 | 32.2 | 32.5 | 32.3 | | | |
| 2 | Cyclobutylmethyl alkyl acetic acids $C_4H_7CH_2CH(COONa)R$ | D 20° | | | | | 37.5 | 33.8 | 31.1 | 29.7 | 31.2 | | | |
| 3 | Cyclopentyl alkyl acetic acids $C_5H_9CH(COONa)R$ | T 25° | | | | 47.0 | 40.1 | 36.6 | 34.7 | 32.2 | | | | |
| 4 | Cyclopentenylethyl alkyl acetic acids $C_5H_7(CH_2)_2CH(COONa)R$ | T 25° | | | 38.2 | 37.9 | 36.7 | 33.2 | 31.5 | 30.4 | 31.2 | | | |
| 5 | Allyl alkyl acetic acids $C_3H_5CH(COONa)R$ | T 25° | | | | | | 36.3 | 32.8 | 30.6 | 31.1 | 31.2 | 33.0 | |
| 6 | Undecylenyl alkyl acetic acids $CH_2{=}CH(CH_2)_9CH(COONa)R$ | T 25° | 35.7 | 33.3 | 30.0 | 28.2 | | | | | | | | |
| 7 | $\alpha,\beta$-Unsaturated acids $C_3H_7CH{=}C(COONa)R$ | T 25° | 47.0 | | | 33.5 | 26.0 | | | | | | | |
| 8 | $\alpha$-Hydroxy acids $R(CH_2)_8CH(OH)COONa$ | D 20° | | 45.5 | 50.6 | 53.0 | 56.5 | 60.0 | | | | | | |
| 9 | $CH_3CH(COONa)R$ | D 20° | | | | | | | | | | 28.2 | 25.8 | 25.0 |
| | | T 25° | | | | | | | | | 31.5 | 28.3 | 27.8 | 26.2 |
| 10 | $C_2H_5CH(COONa)R$ | D 20° | | | | | | | | | 29.3 | 27.4 | 29.6 | |
| | | T 25° | | | | | | | | 33.5 | 30.3 | 29.9 | 29.5 | |
| 11 | $C_3H_7CH(COONa)R$ | D 20° | | | | | | | | 29.8 | 27.5 | 29.3 | | |
| | | T 25° | | | | | | | 35.8 | 31.8 | 30.1 | 29.0 | 33.5 | |
| 12 | *iso*-$C_3H_7CH(COONa)R$ | D 20° | | | | 54.7 | | | | | | | | |
| | | T 25° | | | | 54.6 | | | | | | | | |
| 13 | $C_4H_9CH(COONa)R$ | D 20° | | | 54.6 | 51.4 | 38.8 | | 30.8 | 28.0 | 28.2 | | | |
| | | T 25° | | | 55.4 | 52.3 | 44.2 | | 31.7 | 30.8 | 29.3 | | | |

TABLE I (*Concluded*)

| | R = | | $C_4H_9$ | $C_5H_{11}$ | $C_6H_{13}$ | $C_7H_{15}$ | $C_8H_{17}$ | $C_9H_{19}$ | $C_{10}H_{21}$ | $C_{11}H_{23}$ | $C_{12}H_{25}$ | $C_{13}H_{27}$ | $C_{14}H_{29}$ | $C_{15}H_{31}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14 | $C_5H_{11}CH(COONa)R$ | D 20° | | 55.0 | | 43.4 | | 32.5 | 28.4 | 28.3 | | | | |
| | | T 25° | | 54.5 | 53.4 | 43.9 | 38.7 | 34.4 | 30.5 | 30.0 | 31.2 | | | |
| 15 | $C_6H_{13}CH(COONa)R$ | D 20° | | | | | 31.9 | 27.2 | 26.7 | | | | | |
| | | T 25° | | | 42.4 | 38.0 | 33.8 | 28.1 | 27.9 | | | | | |
| 16 | $C_7H_{15}CH(COONa)R$ | D 20° | | | | 31.7 | 27.6 | 25.6 | | | | | | |
| | | T 25° | | | | 33.7 | 28.0 | 26.8 | 26.1 | | | | | |
| 17 | $C_8H_{17}CH(COONa)R$ | D 20° | | | | | 25.6 | | | | | | | |
| | | T 25° | | | | | 26.5 | | | | | | | |
| 18 | $CH_3CH(CH_3)CH_2CH(COONa)R$ | D 20° | | | | | | | 34.1 | | 29.0 | | | |
| | | T 25° | | | | | | | 32.6 | | 30.4 | | | |
| 19 | $CH_3CH(CH_3)CH(COONa)R$ | D 20° | | | | | | | 33.2 | | | 30.0 | | |
| | | T 25° | | | | | | | 32.3 | | | 30.8 | | |
| 20 | $C_2H_5CH(CH_3)CH(COONa)R$ | D 20° | | | | | | | | | 28.7 | | | |
| | | T 25° | | | | | | | | | 29.5 | | | |
| 21 | $C_3H_7CH(CH_3)CH(COONa)R$ | D 20° | | | | | | | | 28.4 | | | | |
| | | T 25° | | | | | | | | 28.6 | | | | |

T, Tensiometer method; D, Drop-weight method

creased slightly as it reached the middle carbon atom (Fig. 3). The change in surface tension caused by moving the carboxyl group from the end carbon atom to any other carbon atom is not nearly so pronounced in the lower fatty acids. Another interesting phenomenon is that the introduction of an $\alpha$-hydroxyl group into palmitic acid caused the acid to be perfectly soluble in 1:500, yet the solution had a high surface tension, whereas the introduction of an $\alpha$-bromine atom caused the acid to be perfectly soluble in 1:500 and the solution had a low surface tension, yet possessed no appreciable bactericidal action (Table I, No. 8, Table VI).

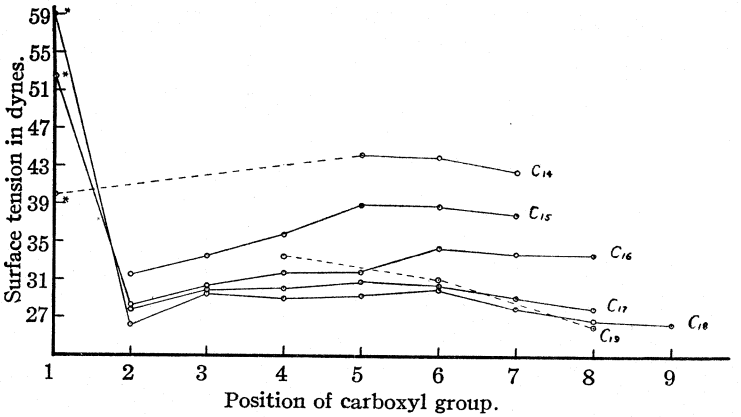


Fig. 3.—Change in surface tension with position of carboxyl group in a number of isomeric fatty acids. * – – Values by Lascaray, *Kolloid. Z.*, **34**, 73 (1924); dilution, 1:500.

The surface tension of solutions of the salts of hydnocarpic and chaulmoogric acids, the acids which constitute the major portion of oils which have been used in the treatment of leprosy, was determined and found to be fairly low (Table II).

## Procedure

The solutions of the sodium salts of the acids for surface tension determinations were prepared in the same manner as the solutions for bacteriological testing. A sample of 0.100 g. of acid was dissolved in ethyl alcohol and neutralized to phenolphthalein with 0.5 *N* sodium hydroxide solution. The solution was then evaporated to dryness and taken up in either 10 or 50 cc. of distilled water. This solution was then diluted and rediluted to the desired concentrations. The media solutions were prepared in the same manner except that 5% glycerol broth was used as a solvent.

The surface tensions of the solutions were determined by the drop-weight method, using the Harkins procedure and corrections and also by means of a du Noüy tensiometer. Duplicate determinations by both

methods on several solutions gave practically identical results. Since the tensiometer method was more rapid it was used for most of the determinations. The tensiometer was especially valuable since it enabled surface tensions on an entire series of acids or dilutions to be determined rapidly and it is believed that the values so obtained are very accurate from a comparative standpoint. Duplicate determinations on the same solution never varied over 0.2 dynes per cm., and duplicate determinations on the same acid at a given concentration seldom varied over 1.5 dynes per cm. The latter includes the experimental error in weighing, diluting and determining the surface tension of duplicate samples of an acid. The values given in the tables are, therefore, accurate to approximately 5% or less. The dilutions of the solutions are indicated at the top of the columns in the tables by notations such as 1:500, which means one part of the sodium salt of the acid in 500 parts of water.

TABLE II

CHANGE OF SURFACE TENSION ON DILUTION

Surface tension in dynes per cm. by tensiometer at 25°

| | 1:100 | 1:500 | 1:1000 | 1:10000 | 1:100000 |
|---|---|---|---|---|---|
| $C_3H_5CH_2CH(COONa)C_{10}H_{21}$ | 34.7 | 32.2 | 35.0 | 42.4 | 45.5 |
| $C_5H_9CH(COONa)C_{10}H_{21}$ | 33.6 | 34.7 | 40.4 | 46.3 | 48.0 |
| $C_5H_7CH_2CH(COONa)C_9H_{19}$ | 33.7 | 33.2 | 37.1 | 48.4 | 53.5 |
| $C_6H_{11}(CH_2)_{10}COONa$ | 36.8 | 32.2 | 32.6 | 36.2 | 51.7 |
| $C_6H_{11}(CH_2)_2CH(COONa)(CH_2)_2C_6H_{11}$ | 34.8 | 42.8 | 47.6 | 53.6 | 57.6 |
| *iso*-$C_3H_7CH(COONa)C_7H_{15}$ | 42.7 | 54.6 | 57.7 | 64.5 | 69.6 |
| $C_5H_{11}CH(COONa)C_5H_{11}$ | 43.7 | 54.5 | 56.8 | 60.7 | 71.1 |
| $CH_3CH(COONa)C_{13}H_{27}$ | 33.4 | 28.3 | 24.6 | 28.6 | 41.3 |
| $C_7H_{15}CH(COONa)C_7H_{15}$ | 26.8 | 33.7 | 38.8 | 49.2 | 50.7 |
| $CH_3CH(CH_3)CH_2CH(COONa)C_{10}H_{21}$ | 33.3 | 32.6 | 35.0 | 42.8 | 46.7 |
| $C_7H_{15}CH(COONa)C_8H_{17}$ | 25.7 | 28.0 | 35.0 | 44.5 | 49.2 |
| $C_7H_{15}CH(COONa)C_9H_{19}$ | 26.0 | 26.8 | 31.8 | 45.8 | 51.6 |
| $C_3H_7CH(COONa)C_{14}H_{29}$ | | 33.5 | 32.2 | 42.9 | |
| $C_5H_{11}CH(COONa)C_{12}H_{25}$ | | 31.2 | 30.2 | 37.0 | |
| $C_7H_{15}CH(COONa)C_{10}H_{21}$ | | 26.1 | 26.4 | 40.8 | |
| $C_3H_5CH(COONa)C_{12}H_{25}$ | 35.0 | 31.1 | 29.0 | 36.0 | 45.0 |
| $CH_2{=}CH(CH_2)_9CH(COONa)C_5H_{11}$ | 32.7 | 33.3 | 35.7 | 48.9 | 53.8 |
| $CH_3(CH_2)_3CH{=}C(COONa)C_7H_{15}$ | 26.3 | 33.5 | 38.9 | 47.8 | 50.5 |
| Hydnocarpic acid | 33.3 | 32.2 | 32.6 | 41.3 | 52.7 |
| Total acids of *Hydnocarpus Wightiana* oil | 31.5 | 30.2 | 30.5 | 37.8 | 59.2 |
| Chaulmoogric acid | 38.2 | 33.1 | 32.8 | 44.9 | 64.7 |

TABLE III

ω-CYCLOHEXYL SUBSTITUTED FATTY ACIDS AND DI-(CYCLOHEXYLALKYL) ACETIC ACIDS

Surface tension in dynes per cm. by tensiometer at 25°; 1:500

| | $x$ = | 0 | 1 | 2 | 2 | 2 | 3 | 6 | 8 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $y$ = | 2 | 2 | 2 | 3 | 4 | 3 | | | | |
| $C_6H_{11}(CH_2)_xCOONa$ | | 53.9 | | | | | | 51.0 | 39.7 | 33.4 | 32.2 | 32.9 |
| $C_6H_{11}(CH_2)_xCH(COONa)(CH_2)_yC_6H_{11}$ | | 52.8 | 49.2 | 42.8 | 37.4 | 34.5 | 33.2 | | | | | |

TABLE IV

CYCLOHEXYL ALKYL ACETIC ACIDS, $C_6H_{11}CH(COONa)R$

Surface tension in dynes per cm.

| R = | $T^a$ 25° 1:500 | $T^a$ 25° 1:1000 | $D^b$ 20° 1:1000 | $D^b$ 20° 1:1000[c] |
|---|---|---|---|---|
| $C_5H_{11}$ | 52.1 | 53.0 | 55.3 | 41.5 |
| $C_6H_{13}$ | 52.3 | 54.7 | 55.1 | 37.2 |
| $C_7H_{15}$ | 37.2 | 43.2 | 42.0 | 35.6 |
| $C_8H_{17}$ | 37.3 | 44.6 | 42.8 | 35.7 |
| $C_9H_{19}$ | 33.5 | 38.5 | 39.0 | 37.8 |
| $C_{10}H_{21}$ | 31.6 | 36.2 | 34.7 | 37.5 |
| $C_{11}H_{23}$ | 31.7 | 33.5 | 33.1 | 39.6 |
| $C_{12}H_{25}$ | 31.5 | 32.5 | 30.9 | 40.2 |

[a] Tensiometer. [b] Drop weight method. [c] 5% Glycerol broth solution.

TABLE V

HEXADECANOIC ACIDS

Surface tension in dynes per cm. by tensiometer

| | 1:100 | 1:500 | $D^a$ 20° 1:500 | $D^a$ 20° 1:500[b] | 1:1000 | 1:10000 | 1:100000 |
|---|---|---|---|---|---|---|---|
| $CH_3CH(COONa)C_{13}H_{27}$ | 33.4 | 28.3 | 28.2 | 22.9 | 24.6 | 28.6 | 41.3 |
| $C_2H_5CH(COONa)C_{12}H_{25}$ | | 30.3 | 29.3 | 24.9 | | | |
| $C_3H_7CH(COONa)C_{11}H_{23}$ | | 31.8 | 29.8 | 28.8 | | | |
| $C_4H_9CH(COONa)C_{10}H_{21}$ | | 31.7 | 30.8 | 30.2 | | | |
| $C_5H_{11}CH(COONa)C_9H_{19}$ | | 34.4 | 32.5 | 31.8 | | | |
| $C_6H_{13}CH(COONa)C_8H_{17}$ | | 33.8 | 31.9 | 30.7 | | | |
| $C_7H_{15}CH(COONa)C_7H_{15}$ | 26.8 | 33.7 | 31.7 | 31.0 | 38.8 | 49.2 | 50.7 |
| $CH_3CH(CH_3)CH_2CH(COONa)C_{10}H_{21}$ | 33.3 | 32.6 | 34.1 | 28.7 | 35.0 | 42.8 | 46.7 |
| $CH_3CH(CH_3)CH(COONa)C_{10}H_{21}$ | | 32.3 | 33.2 | 29.8 | | | |

[a] Drop weight method. [b] 5% Glycerol broth solution.

TABLE VI

MISCELLANEOUS ACIDS

Surface tension in dynes per cm. by drop weight method at 20°

| | 1:500 |
|---|---|
| Total acids of castor oil | 36.6 |
| Soluble reduced castor oil acids | 59.1 |
| Insoluble reduced castor oil acids | 44.7 |
| Dihydroxystearic acid | 40.0 |
| α-Bromopalmitic acid | 30.6 |
| Total acids of cod liver oil | 30.6 |
| $C_6H_{11}(CH_2)_2CH(COONa)CH(COONa)C_4H_9$ | 40.6 |
| $C_6H_{11}CHOH(CH_2)_7COONa$ | 48.3[a] |

[a] Tensiometer at 25°.

## Summary

The surface tensions of aqueous and media solutions of the sodium salts of one hundred and twenty aliphatic acids, previously studied for bactericidal action to *Mycobacterium Leprae* have been determined. It

was shown that without exception all of the bactericidally effective aliphatic acids were marked surface tension depressants. Several general correlations between chemical structure and surface tension depressant action were revealed.

URBANA, ILLINOIS

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[CONTRIBUTION NO. 74 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

# STUDIES OF POLYMERIZATION AND RING FORMATION. XI. THE USE OF MOLECULAR EVAPORATION AS A MEANS FOR PROPAGATING CHEMICAL REACTIONS

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

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Reversible reactions involving the simultaneous formation of a volatile and a non-volatile product are often forced to completion by causing the volatile product to distil from the reaction mixture as fast as it is formed. The purpose of the present note is to call attention to the possibility of extending the application of this principle to instances in which the effective vapor pressure or escaping tendency of a volatile product or potential product is very small. In the molecular still[1] distillation or continuous evaporation can be effected even when the vapor pressure of the distilling substance is as low perhaps as $10^{-5}$ mm. The theory of the process has been discussed by Washburn,[1b] and we need only to mention that successful operation requires a highly evacuated system comprising a condenser placed very close to the evaporating surface. The temperature of the condenser must be low enough to reduce the vapor pressure of the distillate to a negligible value. Under these conditions the mean free path of the molecules is less than the distance from the condenser to the evaporating surface; consequently most of the molecules that manage to escape from the evaporating surface are caught by the condenser with a negligible probability of return.

Mercury and apparently cane sugar can be evaporated in the molecular still at room temperature[1b] and *n*-heptacontane can be distilled without decomposition.[2] The tendency to distil diminishes with increasing molecular weight, and it appears that, so far as practically useful rates are concerned, the upper limit of distillability for paraffin hydrocarbons may lie at as low a molecular weight as 1100 or 1200. For other types of organic compounds it will in general lie at still lower molecular weights.[2] Thus all substances of high molecular weight are practically completely

[1] Brönsted and Hevesy, *Phil. Mag.*, **43**, 31 (1922); (b) Washburn, *Bur. Standards J. Research*, **2**, 476 (1929); (c) Burch, *Proc. Roy. Soc.* (London), **123**, 271 (1929); (d) Hickman, *Chem. Ind.*, **48**, 365 (1929).

[2] Carothers, Hill, Kirby and Jacobson, THIS JOURNAL, **52**, 5279 (1930).

non-volatile. There are many instances of reversible reactions in which only one volatile substance is involved. If this substance has a very low vapor pressure, or if it is strongly held by other substances involved in the reaction, or if its equilibrium concentration is very low, then molecular evaporation may be capable of producing a result not even remotely accessible with the aid of the usual distillation equipment and methods.

Examples of the use of molecular evaporation as a means of propagating chemical reactions are provided in other papers of this series.[3] The reactions involved are reversible bifunctional condensations. The starting materials are linear polymers capable, by self-combination, of yielding a still longer molecule with the elimination of some volatile product. The size of the product molecules depends upon the completeness of the reaction. With the aid of the molecular still one can obtain products of much higher molecular weight than with the ordinary distillation equipment. The same principles can doubtless be applied to other kinds of reversible reactions.

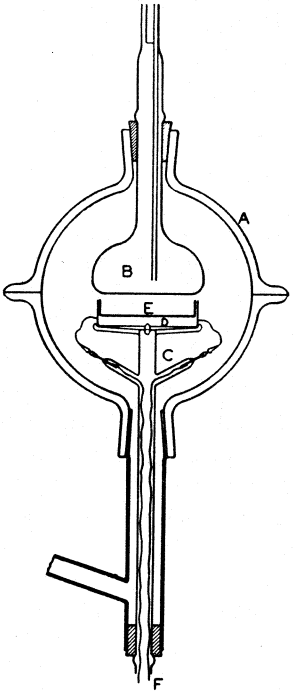


Fig. 1.—Molecular still (1/7 natural size).

The simple stills described by Washburn,[1b] function satisfactorily but they do not provide ready access to the residue from the distillation. For this reason we constructed the instrument shown in Fig. 1 and used it in carrying out some of the reactions referred to above. The new instrument has the advantage that the flat pan containing the distillation residue can be lifted out when the instrument is open.

## Description of the Instrument

The outer shell (A) of the apparatus is made up of two domes from Pyrex vacuum distilling apparatus (Corning Glass Company Catalogue, Item No. 56). The ground surfaces are lubricated with a good vacuum grease. (B) is the condenser provided with water leads. (C) is the glass support for the heater (D) and the distilling pan (E).[4] The heater and distilling pan are contained in an outer copper pan as shown. The heater consists of nichrome wire wound spirally on a sheet of mica which is supported between sheets of thin asbestos

[3] Papers XII, XIII, XIV and XVI.

[4] This pan is conveniently made by cutting a Pyrex beaker close to the bottom. The material of which the pan is composed has a considerable effect on the rate of the bifunctional condensations described in Papers XII, XIII and XIV. No polyesterification could be effected in a copper pan. On the other hand, when superpolyesters and polyanhydrides are prepared in a glass pan the products adhere very firmly to the glass so that the dish is frequently shattered on cooling owing to the force of contraction.

board inserted below the distilling pan. The heater leads (F) are brought up through the support (C) and out as shown. Connection with the heater is made with spring clamps which make the heater readily demountable. The lower part of the apparatus is the regular distilling tube provided with the Pyrex vacuum distilling apparatus (Catalogue No. 56). The rubber stoppers at the top and bottom of the apparatus are well covered with a suitable wax such as picein. A thermocouple (not indicated in the drawing) is led in through the lower wax seal and the junction placed under the pan (E). The slight bulges on the condenser and the pan support where they enter the apparatus are necessary to obviate the danger of these parts sucking in when the apparatus is evacuated.

## Summary

In reversible reactions involving the simultaneous formation of volatile and non-volatile products, the use of molecular evaporation makes it possible to realize chemical effects that cannot be achieved with the aid of the usual distillation equipment. A new design of molecular still is described.

WILMINGTON, DELAWARE

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[COMMUNICATION NO. 75 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

# STUDIES OF POLYMERIZATION AND RING FORMATION. XII. LINEAR SUPERPOLYESTERS[1]

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

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In previous papers we have described polyesters having molecular weights ranging from 800 to 5000 derived from dibasic acids of the series $HOOC(CH_2)_xCOOH$ and glycols of the series $HO(CH_2)_yOH$.[2] These esters are microcrystalline solids that dissolve readily in appropriate solvents. Their solutions are not highly viscous and they show no signs of inherently colloidal behavior. In the present paper we describe polyesters of the same series having much higher molecular weights. They exhibit colloidal behavior and simulate to a remarkable degree some of the properties of certain naturally occurring high polymers. For the sake of brevity and convenience we use the designation $\alpha$-ester or $\alpha$-form for the polyesters having molecular weights ranging from 800 to 5000 and the designation $\omega$-ester or $\omega$-form for the new superpolyesters.

**Nature of the Polyesterification.**—The mutual esterification of dibasic acids and dihydric alcohols is a bifunctional reaction.[3] As such it presents

[1] The term "superpolymer" is applied to linear polymers having molecular weights above 10,000.

[2] (a) Carothers and Arvin, THIS JOURNAL, **51**, 2560 (1929); (b) Carothers and Van Natta, *ibid.*, **52**, 314 (1930); (c) Carothers and Dorough, *ibid.*, **52**, 711 (1930); (d) Carothers, Arvin and Dorough, *ibid.*, **52**, 3292 (1930).

[3] Carothers, *ibid.*, **51**, 2548 (1929).

the formal possibility of yielding (1) cyclic monomeric esters, (2) cyclic polyesters, and (3) open-chain polyesters. Studies already reported have proved that the first possibility is ordinarily realized only in those comparatively rare instances where the nature of the starting material permits the formation of a ring of five or six atoms. Otherwise reaction generally is intermolecular and the product is of the third type. The polyesterification thus consists in a series of intermolecular couplings resulting in the formation of progressively longer chains as indicated by way of illustration in the following equations.

$$\text{HOOC—R—COOH} + \text{HO—R'—OH} \longrightarrow \text{HO—R'—O—CO—R—COOH}$$

$$2\text{HO—R'—O—CO—R—COOH} \longrightarrow \text{HO—R'—O—CO—R—CO—O—R'—O—CO—R—COOH}$$

$$(n+1)\text{HO—R'—O—CO—R—COOH} \longrightarrow \text{HO—R'—O(CO—R—CO—O—R'—O)}_n\text{—CO—R—COOH}$$

The reaction is reversible and an exceedingly large number of entities are involved in the ester equilibrium. The equilibrium can be displaced by the removal of the liberated water, and the more nearly complete the reaction the longer are the molecules of the polyester product. The reaction becomes formally complete when all the molecules of the initial reactants are combined into a single molecule.

A complicating circumstance arises from the fact that the glycol and the acid need not react in precisely equivalent ratio: at any particular stage $n$ molecules of acid may be involved with $n + 1$ molecules of glycol or, conversely, $n$ molecules of glycol may be involved with $n + 1$ molecules of acid. In the former case the product molecules will bear hydroxyl groups at both ends; in the latter they will bear carboxyl groups at both ends. In either event no further progress is possible by esterification. Under favorable conditions, however, coupling may continue nevertheless. Two molecules may unite by a process of ester interchange involving their terminal ester linkages. This mechanism is realized experimentally[2] when di-($\beta$-hydroxyethyl)-succinate (I) is heated *in vacuo*. Glycol is liberated

(I) $\text{HO(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_2\text{COO(CH}_2\text{)}_2\text{OH} + \text{HO(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_2\text{COO(CH}_2\text{)}_2\text{OH} \longrightarrow$
$\text{HO(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_2\text{COO(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_2\text{COO(CH}_2\text{)}_2\text{OH} + \text{HO(CH}_2\text{)}_2\text{OH}$, etc.

and the final product of prolonged heating is the same as one obtained by similarly heating succinic acid with a very small excess of glycol.

The only factor that could theoretically preclude the possibility of producing exceedingly long molecules as the result of bifunctional esterifications is the loss of terminal groups through ring formation. Since in the polyesters thus far examined the terminal groups are still present, it appears that such ring formation does not occur.[4]

[4] Valuable indications in this connection are furnished by Lycan and Adams' studies [THIS JOURNAL, **51**, 625, 3450 (1929)] of the polyesters derived from $\omega$-hydroxydecanoic acid. We should add that our generalization to the effect that no intramolecular reaction occurs in bifunctional esterifications involving compounds whose

Another factor that might be expected to have the same effect is the mutilation of terminal groups, *e. g.*, through the loss of carboxyl as carbon dioxide. But our experience indicates that the loss of terminal groups in this fashion occurs only when patently inappropriate conditions are adopted. More important than this is the fact demonstrated by the behavior of di-(β-hydroxyethyl)-succinate cited above that the coupling can progress through a process of ester interchange involving the last ester linkage. The possibility of further coupling therefore does not absolutely depend upon the integrity of the terminal groups as such.

As a matter of fact, however, as such reactions have been carried out in the past an apparent limit is reached at a comparatively low molecular weight. Thus the glycol and the acid are heated together in a distilling flask provided with a receiver to collect the liberated water, and heating is finally continued at low pressure and considerably elevated temperature. The molecular weight of the polyester product increases during the progress of the heating and finally reaches a value of 3000 to 5000. This value is not noticeably increased if the period of heating is greatly prolonged.

We ascribe the failure of the reaction to progress further under these conditions to the following factors. The concentration of reactive (terminal) groups in esters having molecular weights as high as 3000 is rather low; moreover, such esters are very viscous even at a temperature of 200°. This implies a restricted mobility of the molecules, and a low rate of diffusion of the volatile products to the surface. Beyond this, macromolecular materials, perhaps because of their exaggerated molecular cohesions,[5] have a very powerful tendency to retain dissolved or adsorbed liquids or vapors—several days' heating in high vacuum are required to remove benzene completely from macromolecular polystyrenes or water from resinous esters. All these factors affect either the position of the equilibrium or the rate at which the equilibrium is approached, and one may suppose that if some more drastic and effective means could be found for the removal of water or other volatile reaction products, it would be possible to force the reaction further.

**Methods of Producing Superpolyesters.**—The molecular still, first used by Brönsted and Hevesy[6] for the separation of the isotopes of mercury and later by Washburn[7] for the separation of petroleum hydrocarbons, provides a means for continuously displacing physical equilibria involving

structural units are longer than seven atoms is not altogether free from exceptions. Dr. Van Natta of this Laboratory in preparing polyesters of ω-hydroxydecanoic acid has recently observed the formation of appreciable amounts of the dimeric lactone already obtained by Lycan and Adams by a different method.

[5] Dunkel, *Z. physik. Chem.*, Abt. A, **138**, 42 (1928).

[6] Brönsted and Hevesy, *Phil. Mag.*, **43**, 31 (1922).

[7] Washburn, *Bur. Standards J. Research*, **2**, 476 (1929); see also Burch, *Proc. Roy. Soc.* (London), **123**, 271 (1929); and Hickman, *Chem. Ind.*, **48**, 365 (1929).

very minute vapor pressures, and the application of this to the chemical equilibrium under consideration led to the desired result.

Some of the experiments described below were made in stills of the type described by Washburn[7] and others in a modified still described in the preceding paper,[8] where the principles involved are also briefly discussed.

For reasons of a theoretical nature that need not be discussed, our first experiments were made with an ester which has not been described previously, namely, the trimethylene ester of hexadecamethylene dicarboxylic acid. This was obtained from the acid and the glycol by the method used for other α-polyesters.[2a]

It was then placed in the molecular still and heated by a bath at 200° for a total time of twelve days. During the first seven days a small amount of distillate collected on the condenser. No distillate was observed during the remaining five days. The viscosity of the molten polyester increased progressively during the heating, and the final product showed an apparent molecular weight of about 12,000.

The same treatment applied to ethylene succinate, ethylene sebacate, and to polyesters derived from ω-hydroxydecanoic acid and from ω-hydroxypentadecanoic acid, led to similar transformations.

A part of the effect of the molecular still treatment is evidently due to the greatly prolonged time of heating, and it was found later that a similar, if somewhat less pronounced, effect could be produced by merely heating polyesters such as ethylene sebacate in thin layers at ordinary pressure in a stream of nitrogen for a long period of time, or by bubbling a stream of nitrogen through the molten polyester.

**Physical Properties of Superpolyesters.**—Linear α-polyesters are microcrystalline powders (in certain cases resins) that dissolve readily in certain solvents such as cold chloroform and yield solutions which are quite mobile. The crystalline esters melt fairly sharply and when molten they are exceedingly viscous. On cooling they solidify to opaque masses which range from rather hard, brittle, porcelain-like masses to soft, waxy solids as the length of the polymethylene chain in the acid or glycol from which they are derived increases.

The superpolyesters in the massive state are harder and much tougher. They also dissolve in cold chloroform but the process is slow; they first imbibe solvent and swell, and their solutions are highly viscous. They separate from solution as more or less coherent powdery or curdy masses. When heated they melt at approximately the same temperatures as the α-polyesters from which they are derived. The phenomena associated with the melting, however, are quite different from those observed in the α-polyesters. The solid ester at the melting point suddenly becomes transparent, but it does not lose its shape; a tendency to flow appears only at a

[8] Paper XI.

considerably higher temperature. In the solid state the superpolyesters furnish sharp x-ray powder diffraction patterns that closely resemble similar patterns obtained from the corresponding $\alpha$-polyesters. At a temperature a few degrees below the melting point the patterns lose their sharpness. At the melting point the pattern is a diffuse halo characteristic of a liquid. The most remarkable property of the superpolyesters is their capacity to be drawn out into very strong, pliable, highly oriented fibers, and this is discussed in detail in a subsequent paper.[9]

By way of summary, the properties of the $\alpha$- and $\omega$-polyesters from trimethylene glycol and hexadecamethylene dicarboxylic acid are listed in Table I. Similar relations exist between the $\alpha$- and the $\omega$-forms of other polyesters. One curious property of the $\omega$-esters deserves special mention. They adhere very firmly to the glass vessel (in the molecular still) in which they are prepared, and the force of contraction during cooling often causes the vessel to be completely shattered if the layer of ester is more than two or three millimeters thick.

TABLE I

PROPERTIES OF $\alpha$- AND $\omega$-POLYESTERS FROM TRIMETHYLENE GLYCOL AND HEXADECAMETHYLENE DICARBOXYLIC ACID

| | $\alpha$-Ester | $\omega$-Ester |
|---|---|---|
| Apparent mol. wt. | 3000 | 12,0000 |
| At 100° C. | Viscous liquid | Soft, sticky resin |
| At room temperature | White, opaque, brittle wax; $d_{20}^{20}$ 1.061 | Cream colored, opaque, horny, elastic; $d_{20}^{20}$, 1.058 |
| Melting point, °C. | 75–76 | Becomes transparent at 75, but does not flow |
| Solubility | Very soluble in cold $CHCl_3$. Readily soluble in hot ethyl acetate; separates on cooling as a microcrystalline powder | Swells in cold $CHCl_3$, then dissolves. Swells and slowly dissolves in hot ethyl acetate; separates on cooling as a white, amorphous, curdy precipitate |
| Relative viscosity of 7.3% weight solution in chloroform (chloroform, 2.16 seconds = 1 unit) | 8.6 units | 166 units |

## Structure of the $\omega$-Polyesters

The simplest and most reasonable assumption concerning the superpolyesters is that they are formed by a continuation of the same bifunctional esterification that first results in the formation of the $\alpha$-polyesters, and that they are exceedingly long polymeric chains bearing hydroxyl or carboxyl groups at the ends. Their physical, chemical and analytical behavior is completely consistent with this assumption, but no actual data

[9] Paper XV.

on the presence of terminal groups are yet available. The average length of the molecules also is still very uncertain. The molecular weights quoted in Table I were obtained by ebullioscopy and in view of the fact that the observed elevations did not greatly exceed the experimental error they can be accepted as signifying only that the molecular weights are quite large—at least as high as 10,000. Comparison of physical properties indicates that molecular weights of the ω-polyesters probably lie in the neighborhood of 20,000. Further work on the determination of the molecular weights of the superpolyesters is in progress.

**ω-Trimethylene Ester of Hexadecamethylene Dicarboxylic Acid.**—This ester was obtained in its α-form by heating the acid together with a 10% excess of the glycol in a distilling flask at 180–200° for three hours, and then heating the residue to 200° for six hours at a pressure less than 1 mm. It was thus obtained in the form of a very viscous liquid which on cooling solidified to a hard, waxy mass. It was readily soluble in cold chloroform and in hot ethyl acetate, from which it separated on cooling as a white microcrystalline powder. It melted rather sharply at 75–76°. Its apparent molecular weight was about 3300.

*Anal.* Calcd. for $-O-(CH_2)_3-O-CO-(CH_2)_{16}-CO-$ = $C_{21}H_{38}O_4$: C, 71.13; H, 10.81; saponification equivalent, 177.2; mol. wt. 354.3. Calcd. for $H(-O-(CH_2)_3-O-CO-(CH_2)_{16}-CO-)_{10}-O(CH_2)_3-OH = C_{213}H_{388}O_{42}$; C, 70.63; H, 10.80; saponification equivalent, 181; mol. wt. 3619. Found: C, 70.34, 70.40; H, 10.60, 10.69; saponification equivalent, 175.2; mol. wt. (in boiling benzene), 3600, 3200.

A sample (8.5 g.) of this recrystallized ester was placed in a molecular still of the type described by Washburn.[10] The condenser was cooled with running tap water, and a trap between the mercury diffusion pump and the still was cooled with liquid air. The still was heated by means of a metal bath kept at about 200°. The pressure of the system as measured by a McLeod gage between the trap and the pump was always less than $10^{-5}$ mm. Heating was continued for seven days. During the first two days of heating, 0.4 g. of distillate collected on the condenser. This was removed and the heating of the residue was continued for five days more. No distillate collected during this period.

The analytical composition and the saponification equivalent of the residual ester were the same as those of the starting material. Its molecular weight, however, was much greater.

*Anal.* Calcd. for $-O-(CH_2)_3-O-CO-(CH_2)_{16}-CO-$ = $C_{21}H_{38}O_4$: C, 71.13; H, 10.81; saponification equivalent, 177.2; mol. wt. 354.3. Calcd. for $H-(O-(CH_2)_3-O-CO-(CH_2)_{16}-CO)_{34}-O-(CH_2)_3-OH = C_{717}H_{1300}O_{258}$: C, 70.89; H, 10.83; saponification equivalent, 178.2; mol. wt., 12,122. Found: C, 70.38, 70.52; H, 10.56; 10.53; saponification equivalent, 178.4; mol. wt. (in boiling benzene) 12,100.

The distillate was not homogeneous. By crystallizing it from alcohol there was obtained an apparently homogeneous fraction composed of needles melting sharply at 124–125°. It depressed the melting point of hexadecamethylene dicarboxylic acid (which melts at 122–123°) and was neutral. A single ultimate analysis indicated that it was possibly a monomeric form of the trimethylene ester of hexadecamethylene dicarboxylic acid.

*Anal.* Calcd. for $O-(CH_2)_3-O-CO-(CH_2)_{16}-CO$; C, 71.13; H, 10.81. Found: C, 70.06; H, 10.63.

[10] Washburn, *Bur. Standards J. Research*, **2**, 480 (1929).

A sample of the α-ester and heated at 200–250° for thirty-two hours with a current of dry nitrogen bubbling through the molten mass. The viscosity of the molten polymer increased very greatly and the product exhibited the phenomenon of cold-drawing described in paper XV.

**ω-Polyethylene Succinate.**—A sample of polyethylene succinate having the approximate formula $HO—(CH_2)_2—O(CO—(CH_2)_2—CO—O—(CH_2)_2—O)_{21}—H$[11] was heated in the molecular still as described above for the trimethylene ester of hexadecamethylene dicarboxylic acid. From the very small amount of distillate no homogeneous fraction could be isolated. The residue was a tough, horny, somewhat elastic mass (the original material was hard, brittle, rather porcelain-like). On being heated to 97° it softened to a very viscous and somewhat rubbery mass. Fibers prepared from this material were short and rather brittle.

*Anal.* Calcd. for $C_6H_8O_4$: C, 50.00; H, 5.50. Found: C, 50.30; H, 5.70.

**ω-Polyester from ω-Hydroxydecanoic acid.**—ω-Hydroxydecanoic acid was prepared by the method of Lycan and Adams.[12] Five grams was heated under a moderate vacuum for ten hours to bring about incipient polymerization. If this is neglected and the acid heated directly in the molecular still, it distils practically completely before polymerization sets in. The material after the preliminary heating was transferred to the molecular still and heated at 150° for twenty-four hours. Two and four-tenths grams of distillate (m. p. 60–65°) collected. This was not further examined. The residue was a hard brittle wax which was heated for four days more at 150° and then at 200° for two days. The final residue was a light gray, translucent, tough, flexible mass. On being heated it suddenly became transparent at 65° but did not lose its shape. At higher temperatures it could easily be drawn into threads which could be cold drawn.

**Microscopic Observation at a Magnification of 180 Diameters.**—A thin hazy film was obtained by placing a small specimen of the ester on a slide and covering it with a cover glass. Between crossed nicols the field appeared as an aggregate of very small, irregular anisotropic particles, each of which showed two extinction positions. The slide was then warmed to melt the ester and the cover glass moved about 5 mm. The middle region of the specimen when cold was now transparent and homogeneous; the surrounding portions were unchanged. This effect is apparently due to the action of stress in moving the slide. The transparent section showed brilliant interference colors between crossed nicols and extinction parallel and normal to the direction of the stress applied.

*Anal.* Calcd.: C, 70.59, H, 10.59. Found: C, 70.24, 70.21; H, 10.74, 10.79; mol. wt. in boiling ethylene chloride, 24,600.

**ω-Ester from ω-Hydroxypentadecanoic Acid.**—One gram of "exaltolide" (the lactone of ω-hydroxypentadecanoic acid) was refluxed with 0.5 g. of sodium hydroxide in 12 cc. of water and 5 cc. of alcohol for five hours. The solution was evaporated to dryness on a steam-bath, dissolved in 450 cc. of water, acidified with dilute sulfuric acid, and extracted with ether. The ether solution was dried over magnesium sulfate, filtered, and evaporated to dryness; yield, 1.075 g. The product was recrystallized from benzene; m. p. 83–84°. The acid was put in the molecular still and heated overnight at 150°. It distilled completely except for a very small residue of hard wax. The distillate was heated for six hours at 150° at 1 mm. and again placed in the still and heated for seven days. A small amount of distillate which melted at 70–75° was not further examined.

The residue consisted of 0.65 g. of a flexible, translucent mass. It became transparent at 95°, yielding a stiff mass which held its shape up to 200°. It could be drawn into thin fibers and cold drawn.

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[11] Carothers and Dorough, THIS JOURNAL, **52**, 711 (1930).

[12] Lycan and Adams, *ibid.*, **51**, 625 (1929).

**Ethylene Sebacate.**—101 g. (0.5 mole) of sebacic acid and 32.5 g. (0.525 mole) of ethylene glycol were heated together at atmospheric pressure in a Claisen flask at 175°. The aqueous distillate was discarded. The residue was then heated at 250° for five hours at 2 mm. pressure. The light gray-buff product was a hard wax. Threads drawn from the molten ester, if pulled immediately while still warm, yielded transparent fibers. The product after recrystallization from ethyl acetate melted at 75° (copper block) and still exhibited the cold drawing phenomenon; molecular weight by cryoscopic method in benzene, 4800, 6000.

## Summary

By prolonged heating in a molecular still or in a stream of inert gas, the previously described linear polyesters derived from dibasic acids and glycols or from higher ω-hydroxy acids are caused to react with themselves to produce polyesters of much higher molecular weight. The new superpolyesters (ω-polyesters) are tough, opaque solids which exhibit sharp x-ray powder diffraction patterns and become transparent at a definite temperature. They dissolve in chloroform to form highly viscous solutions. The mechanism of the reaction is discussed.

WILMINGTON, DELAWARE

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[COMMUNICATION NO. 76 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

# STUDIES OF POLYMERIZATION AND RING FORMATION. XIII. POLYAMIDES AND MIXED POLYESTER-POLYAMIDES

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

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Above its melting point ϵ-aminocaproic acid undergoes dehydration with the simultaneous formation of two different products.[1] One of these is the cyclic lactam, a seven-membered ring. The other is a polyamide having the formula

$$\cdots\text{—NH—}(CH_2)_5\text{—CO—NH—}(CH_2)_5\text{—CO—NH—}(CH_2)_5\text{—CO—}\cdots$$

This compound is analogous to the polyesters obtained by the self-esterification of higher hydroxy acids or by the action of glycols on dibasic acids. The binding atom between the units in the case of the esters is —O— and in the case of the polyamide —NH—. In comparison with the esters the polyamide is harder, tougher, less easily fusible and much less soluble. The difference lies in the direction required by the much higher molecular cohesions of amides as compared with esters.[2]

The polyamide prepared by dehydration of the amino acid at atmospheric pressure or under diminished pressure in the usual distillation equipment has an apparent molecular weight of about 1000 (the actual value probably

[1] Carothers and Berchet, THIS JOURNAL, **52**, 5289 (1930); Gabriel and Maass, *Ber.*, **32**, 1266 (1899); Braun, *ibid.*, **40**, 1835 (1907).

[2] Dunkel, *Z. physik. Chem., Abt. A*, **138**, 42 (1928).

lies somewhat higher than this, perhaps in the neighborhood of 3000). It corresponds, therefore, in molecular weight with the $\alpha$-polyesters that have been described in previous papers.[3] The polyesterification reaction can be forced further toward completion by the use of molecular distillation, and this process leads to the formation of superpolyesters described in the preceding paper.[4] One of the objects of the experiments described in the present paper was to examine the possibility of forcing the amide reaction in a similar manner so as to obtain a polyamide of very high molecular weight.

The polyamide already described was placed in the molecular still and heated for forty-eight hours at 200°. A very small amount of the crystalline cyclic lactam distilled from the reaction mixture and the residue was considerably changed in its properties. It was harder and tougher than before and in thin sections was flexible and elastic. It softened at 210° with considerable decomposition. Like the initial amide it was insoluble in common organic solvents with the exception of hot phenol and hot formamide.

*Anal.* Calcd. for $C_6H_{11}ON$: C, 63.71; H, 9.73. Found: C, 63.94, 63.94; H, 9.72, 9.76.

The change in properties indicates a considerable increase in molecular weight but no actual measurements of molecular weight are available owing to the lack of any method of sufficient reliability.

The superpolyesters described in the preceding paper are especially interesting because of their ability to furnish strong, pliable, highly oriented fibers. This property is discussed in detail in Paper XV. As synthetic silk, however, these materials suffer from the defect of low melting point and considerable solubility in various organic solvents. On the other hand, the polyamide described above is too infusible and insoluble to allow a ready test of its ability to furnish fibers. In the hope of obtaining a compromise between the properties of the polyesters and the polyamides we prepared mixed polyester-polyamides. These compounds were obtained by heating together trimethylene glycol, hexadecamethylene dicarboxylic acid and $\epsilon$-aminocaproic acid. The glycol was used in a 5% excess over the amount equivalent to the dibasic acid and the amino acid was varied in different experiments in the proportion of 1, 2, 3 and 5 moles per mole of dibasic acid. The mixtures were separately heated in a Claisen flask for three hours in a current of dry nitrogen by means of a bath kept at 200–220°. Heating was continued for five hours more at a pressure of 1 mm. with the bath at 250–260°. The very viscous residue was then removed from the flask and transferred to the molecular still, where it was heated for three days at 200°. So far as could be inferred from the

[3] Carothers and Arvin, THIS JOURNAL, **51**, 2560 (1929); Carothers and Van Natta, *ibid.*, **52**, 314 (1930).

[4] Paper XII.

physical appearance of these products the molecular still treatment produced very little effect although in each experiment a small amount of the cyclic lactam from the amino acid was obtained as a distillate.

The products were opaque or translucent solids, hard, very tough, and in thin sections flexible and elastic. As the proportion of amino acid increased, the polymers increased in brittleness, hardness, transparency and melting point. The effect of the composition on melting point is indicated below:

| | | | |
|---|---|---|---|
| 1 mole of amino acid | *ca.* 73° | 3 moles of amino acid | 125° |
| 2 moles of amino acid | 100° | 5 moles of amino acid | 145° |

The melting points were determined on a copper block. In the two polymers of lowest amino acid content the temperatures at which the specimens became transparent were taken as the melting points. In the other two cases where the high degree of transparency when cold made this determination extremely uncertain the temperatures at which the sample first began to adhere slightly to the block were taken as the melting points.

The solubility of the mixed polyester-polyamides also diminished with increasing amino acid content. The first member of the series was swelled by hot ethyl acetate and finally completely dissolved. It separated from the cold solution in the form of soft powder. The second was very slightly soluble in hot ethyl acetate, and the higher members were practically insoluble. Since the polyamide derived from ϵ-aminocaproic acid is not dissolved by hot ethyl acetate, the mixed polyester-polyamides are evidently not merely physical mixtures. From the nature of the reaction also it seems likely that all the components participate in forming each molecule of the product. The different units that may be present in the product molecules are

$$\text{—NH—R—CO—} \qquad \text{—O—R′—O—} \qquad \text{—CO—R″—CO—}$$

which may be joined in any order that leads to ester or amide linkages.

The mixed polyester-polyamides when molten can readily be drawn out into filaments by touching a specimen with a rod and drawing the rod away. The successful production of continuous filaments by this method requires a degree of plasticity in the molten mass that appears only at a temperature somewhat above the melting point. Filaments obtained in this way are brittle and opaque. When slightly warmed (*e. g.*, to 40 to 50°) they can be drawn out by the action of stress into transparent fibers which are exceedingly pliable. Purely qualitative observations indicate that these fibers are considerably stronger than similar fibers derived from the ω-polyesters.

## Summary

The polyamide derived from ϵ-aminocaproic acid when heated in the molecular still undergoes a considerable change in its physical properties,

indicating an increase in molecular weight. By heating together ϵ-aminocaproic acid with hexadecamethylene dicarboxylic acid and trimethylene glycol, mixed polyester-polyamides are obtained. These materials in their physical properties lie between the polyesters and the polyamides and like the superpolyesters described in the preceding paper they can be drawn out into strong, pliable, transparent fibers.

WILMINGTON, DELAWARE

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[COMMUNICATION NO. 77 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & CO.]

# STUDIES OF POLYMERIZATION AND RING FORMATION. XIV. A LINEAR SUPERPOLYANHYDRIDE AND A CYCLIC DIMERIC ANHYDRIDE FROM SEBACIC ACID

BY JULIAN W. HILL AND WALLACE H. CAROTHERS

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In a previous paper[1] it has been shown that adipic anhydride as ordinarily prepared is a linear polymer of the type formula represented by I and that under the action of heat *in vacuo* it is broken down to the cyclic monomer, a seven-membered ring.

(I) $\cdots O—CO—R—CO—O—CO—R—CO—O—CO—R—CO—\cdots$

Observations have now been extended to sebacic anhydride, and it is shown that the anhydride ($\alpha$-anhydride) prepared by the action of acetic anhydride or acetyl chloride on sebacic acid is also polymeric. No smooth depolymerization of this polymer can be effected under ordinary conditions, but in the molecular still[2] at elevated temperatures two processes occur simultaneously. The $\alpha$-anhydride is transformed into a polyanhydride of much higher molecular weight ($\omega$-anhydride) and at the same time depolymerization occurs with the formation of a crystalline product ($\beta$-anhydride), which is shown to be not the eleven-membered cyclic monomer, but the twenty-two membered cyclic dimer. At its melting point the dimer reverts to a higher polymer ($\gamma$-anhydride). The anhydrides of different origins are arbitrarily assigned the prefixes $\alpha$, $\beta$, $\gamma$ and $\omega$ to designate them for the purposes of discussion.

**Sebacic $\alpha$-Anhydride.**—Voerman[3] obtained this as a microcrystalline solid melting at 74.5° by the action of acetyl chloride on sebacic acid. He seemed unable to decide whether to regard it as monomeric or polymeric. Compared with succinic and glutaric anhydrides (known to be monomeric) it showed a diminished solubility and ability to crystallize, and molecular weight determinations in boiling benzene and boiling acetone gave ab-

[1] J. W. Hill, THIS JOURNAL, **52**, 4110 (1930).

[2] Paper XI.

[3] Voerman, *Rec. trav. chim.*, **23**, 265 (1904).

normally high values. The doubt concerning its polymeric character arose from the fact that freezing point determinations in phenol gave values agreeing with those calculated for the monomer, but Voerman overlooked the fact that sebacic anhydride reacts very rapidly with phenol to give phenyl esters of sebacic acid.

We prepared the $\alpha$-anhydride by heating sebacic acid with excess acetic anhydride, distilling off the volatile material, and precipitating a benzene solution of the residue with petroleum ether. The melting points varied somewhat from one preparation to another and a typical specimen melted at 79–80°. The molten anhydride is exceedingly viscous; on cooling it crystallizes: minute doubly refracting spherulites first separate and grow to what appear to be star-like clusters of needles. This behavior is highly characteristic of crystalline linear high polymers and is observed with such diverse materials as polyesters,[4] trimethylcellulose,[5] and triacetylinulin.[6]

At a temperature of 200° and under a pressure of 0.1 mm. the $\alpha$-anhydride shows no tendency to distil, and this behavior is also consistent with a highly polymeric structure.

We tentatively assign to sebacic $\alpha$-anhydride the formula II.

(II) $CH_3CO—[—O—CO—(CH_2)_8—CO—]_x—O—CO—CH_3$

This represents it as a linear polymer and the chains are terminated by acetyl groups derived from the reagent used in bringing about the anhydride formation. It reacts with water to form sebacic acid and acetic acid. The latter may conceivably represent adsorbed acetic acid or acetic anhydride not removed in the purification process, but we are inclined to the view that it arises from acetyl groups that actually form a part of the polyanhydride molecule. This assumption together with the estimation by distillation and titration of the amount of acetic acid formed on hydrolysis furnished a value of 5260 for the molecular weight of a typical specimen of the polymer.

A specimen of the recrystallized $\alpha$-anhydride which had been stored for three days in a vacuum desiccator over phosphorus pentoxide, potassium hydroxide, and paraffin was refluxed with 3 g. of sodium hydroxide in 40 cc. of water, diluted, acidified with sulfuric acid, and distilled with the occasional addition of water. A total of 415 cc. of distillate was collected and titrated with 0.1 *N* sodium hydroxide. Sodium acetate was identified in the resulting neutralized solution by microscopic observation of the highly characteristic crystals of sodium uranyl acetate formed upon adding uranyl nitrate. We are indebted to Mr. W. D. M. Bryant for this identification. Since it was found that sebacic acid itself tends to steam distil very slowly, a correction was made by repeating the above determination using 6 g. of pure sebacic acid.

*Anal.* Subs. 5.51 g.: 0.0999 *N* NaOH, 26.35 cc. Blank: 0.0999 *N* NaOH, 5.35 cc. Found: (assuming two acetyl groups per molecule) mol. wt., 5260.

[4] Carothers and Arvin, THIS JOURNAL, **51**, 2560 (1929).

[5] Hess, "Die Chemie der Cellulose," Akademische Verlagsgesellschaft, Leipzig, 1928, p. 432.

[6] Pringsheim and Hensel, *Ber.*, **63**, 1096 (1930).

A different though not strictly independent estimate of molecular weight is found in the quantitative analysis of the behavior of the polymer toward aniline, which is described in the next section, and this method gives a value of 5500. Attempted molecular weight determinations in boiling benzene gave much lower values than this (as low as 650), but their lack of constancy and reproducibility deprives them of any significance.[7] On the other hand, the $\alpha$-anhydride in its physical properties closely resembles polyesters derived from sebacic acid and known to have molecular weights in the neighborhood of 5000.

The analytical data presented below are consistent with the suggested structure for the $\alpha$-anhydride.

| | Calcd., % | | Found, % | |
|---|---|---|---|---|
| | C | H | C | H |
| $(C_{10}H_{16}O_3)_n$ | 65.18 | 8.75 | 64.19 | 9.07 |
| $CH_3COO(C_{10}H_{16}O_3)_3COCH_3$ | 62.35 | 8.31 | 64.22 | 9.01 |
| $CH_3COO(C_{10}H_{16}O_3)_8COCH_3$ | 64.00 | 8.57 | | |
| $CH_3COO(C_{10}H_{16}O_3)_{30}COCH_3$ | 64.84 | 8.71 | | |

**Behavior of Sebacic Anhydrides toward Aniline.**—Theory requires a difference, both qualitative and quantitative, between cyclic monomeric anhydrides and linear polymeric anhydrides in their behavior toward unsymmetrical reagents such as aniline. This requirement was first pointed out by one of us and experimentally verified in the case of adipic anhydrides.[1,8] The analysis has now been extended and further observations made with sebacic anhydrides.

The monomeric anhydride (II) can react with aniline to form only a single product, namely, the monoanilide of sebacic acid.

[7] The low and inconsistent molecular weight values obtained for the polymeric anhydrides in boiling benzene are probably due to progressive degradation by hydrolysis. Greer has lately shown [THIS JOURNAL, **52**, 4191 (1930)] that completely dry benzene seizes with great avidity sufficient moisture to provide 0.000229 g. of water for one gram of benzene. In a molecular weight determination this would be sufficient to furnish more than one gram of water for each 100 g. of anhydride. The hydrolytic absorption of water in this proportion (1:100) would reduce the average molecular weight of the anhydride by 75% if the initial value were 5400 and the polymer were an open chain. If the initial value were 396 the reduction would be only 14%. If the polymer were cyclic its molecular weight might actually be slightly increased by partial hydrolysis.

[8] We now find that Étaix [*Ann. chim.*, [7] **9**, 356 (1896)] has recorded the fact that the anhydrides of adipic, suberic, azelaic and sebacic acids react with ammonia to give the diamides as well as the amic acids. Einhorn and Diesbach [*Ber.*, **39**, 1222 (1906)] have also observed that the anhydrides of diethylmalonic acid react with ammonia and with diethylamine to form both diamides and amic acids. But apparently none of these investigators recognized the bearing of this behavior on the structure of the anhydrides. Incidentally, it seems certain in view of this behavior that Einhorn and Diesbach's tetrameric diethylmalonic anhydride is actually a sixteen-membered ring. On the other hand, their dodecamer is probably a high polymeric mixture rather than a definite individual.

(II) $\ulcorner\!\!-CO-(CH_2)_8-CO-O-\!\!\urcorner + C_6H_5NH_2 \longrightarrow C_6H_5NH-CO-(CH_2)_8-COOH$

In the polymeric form, however, as soon as one anhydride linkage reacts with aniline, reaction at the next linkage will give different products depending upon which side of the oxygen is involved with the reagent. In III we symbolize aniline (RNH—H) as b—a.

(III) $\ldots-CO-(CH_2)_8-CO-O-CO-(CH_2)_8-CO-O-CO-(CH_2)_8-CO-O-\ldots$

$$\begin{array}{ccc} \vdots & & \vdots \\ b.a & \longrightarrow & b.a \\ \vdots & & \vdots \\ & & a.b \\ & & \vdots \\ a.b & \longrightarrow & b.a \\ & & \vdots \\ & & a.b \end{array}$$

Considering the two linkages of an interior unit of the chain, if reaction occurs in the direction b—a at the first one it may occur in the directions b—a, and a—b at the second; and if the direction is a—b at the first it may be either b—a or a—b at the second. If we assume that reaction is random, *i. e.*, that the direction of reaction at the second linkage is not affected by the direction that the reaction has already taken at the first linkage, then the probability of each of these four possibilities is the same, and the terminal groups attached to the reaction product derived from the unit under consideration are (1) a b, (2) a a, (3) b b and (4) b a. The first and fourth of these represent monoanilide, and the second and third represent, respectively, dibasic acid and dianilide. Thus each interior unit of the anhydride chain will yield

$^1/_4$ molecule of dibasic acid
$^1/_4$ molecule of dianilide, and
$^1/_2$ molecule of monoanilide

and this total product will contain one atom of acid hydrogen.

If the polyanhydride is cyclic, all the units are interior units, and the ratio of products indicated above will be maintained so long as the anhydride is polymeric (*i. e.*, not monomeric). But if the chains are open this ratio will be modified.

We consider the case IV in which the chains are open and terminated by carboxyl groups.

(IV) $HOOC-(CH_2)_8-CO-O-[-CO-(CH_2)_8-CO-O-]_{x-2}-CO-(CH_2)_8-COOH$

The total number of units in the chain is $x$. Of these, the $x$-2 interior units will furnish acid, monoanilide and dianilide in the ratios already indicated, while the terminal units will each furnish one-half molecule of acid and one-half molecule of monoanilide. Thus the total products are

$(x - 2)/4 + 1$ molecule of dibasic acid
$(x - 2)/2 + 1$ molecule of monoanilide, and
$(x - 2)/4$ molecules of dianilide

and the number of atoms of acidic hydrogen in the product is

$$[(x - 2)/4 + 1]\,2 + (x-2)/2 + 1 = x + 1$$

If $M$ is the gram molecular weight of the polymer, then, since the molecular weight of the structural unit is 184

$$184x + 18 = M \qquad (1)$$

and this weight after reacting with aniline will furnish $x + 1$ mole of hydrogen ion. Thus the weight of anhydride required to furnish one mole of hydrogen ion is

$$M/(x + 1) \qquad (2)$$

Let g represent the weight of a sample of polyanhydride of the formula IV which is treated with aniline and cc represent the volume in cubic centimeters of normal alkali required to neutralize the product. Then from (2)

$$M/(x + 1) = 1000\ \text{g}(/\text{cc}) \qquad (3)$$

and from (1)

$$x = (M - 18)/184 \qquad (4)$$

Substituting and solving for $M$, we have

$$M = 166{,}000\ \text{g}/(184\ \text{cc} - 1000\ \text{g}) \qquad (5)$$

If the terminal groups are acetyl as in V

(V) $CH_3CO—O—[—CO—(CH_2)_8—CO—O]_x—COCH_3$

$M = 184 + 102$, and this weight after reacting with aniline will furnish

$x/4$ moles of dibasic acid
$x/4$ moles of dianilide
$x/2$ moles of monoanilide
1 mole of acetic acid, and
1 mole of acetamide

The moles of available hydrogen ion in this product are

$$2x/4 + x/2 + 1 = x + 1$$

In this case equation (5) becomes

$$M = 82{,}000\ \text{g}/(184\ \text{cc} - 1000\ \text{g}) \qquad (6)$$

The manner in which the calculated available acid from the aniline reaction product varies with the molecular weights of different sebacic anhydrides is indicated in Table I.

From the data of Table I it is evident that even if one allows an error of 2% in the titration it should be possible to distinguish an open chain terminated by carboxyl and having a molecular weight of 7500 or less from a cyclic anhydride. If the terminal groups of the chain are acetyl, a similar distinction is possible only if the molecular weight lies below about 3500.

TABLE I

ACID FURNISHED BY ANILINE REACTION PRODUCT OF SEBACIC ANHYDRIDES

| Structural units | Mol. wt. (for cyclic anhydride) | Millimoles of available $H^+$ in reaction product from one gram of anhydride: Cyclic anhydride | Chain terminated by carboxyl | Chain terminated by acetyl |
|---|---|---|---|---|
| 1 | 184 | 5.44 | 9.9 | 6.95 |
| 2 | 368 | 5.44 | 7.75 | 6.39 |
| 3 | 552 | 5.44 | 7.02 | 6.12 |
| 4 | 736 | 5.44 | 6.62 | 5.97 |
| 6 | 1,104 | 5.44 | 6.24 | 5.82 |
| 10 | 1,840 | 5.44 | 5.92 | 5.66 |
| 15 | 2,760 | 5.44 | 5.76 | 5.59 |
| 20 | 3,680 | 5.44 | 5.68 | 5.55 |
| 40 | 7,360 | 5.44 | 5.56 | 5.49 |
| 60 | 11,040 | 5.44 | 5.52 | 5.48 |
| 100 | 18,400 | 5.44 | 5.49 | 5.46 |
| 200 | 36,800 | 5.44 | 5.46 | 5.45 |

The data from which the molecular weight of the α-polyanhydride described in the preceding section were calculated are as follows.

Weighed samples of the reprecipitated anhydride, which had been stored for several days in an evacuated desiccator over solid potassium hydroxide, were added to 5 to 8 cc. of aniline and triturated with a stirring rod until a smooth cream was formed. The mixture was then diluted with about 30 cc. of 95% alcohol and titrated with 0.1 *N* sodium hydroxide using phenolphthalein as the indicator.

*Anal.* Subs. 0.5869, 0.4814, 0.5632: 0.0999 *N* NaOH, 32.40, 26.55, 31.12 cc. Calcd. by equation (6): $M$ = 5532, 5891, 5248.

**Sebacic ω-Anhydride.**—Attempts to depolymerize sebacic α-anhydride by heating it under greatly diminished pressure in a Claisen flask resulted merely in thermal decomposition with the formation of tarry products. But in the molecular still,[9] at 200° change occurred simultaneously in two directions: a crystalline distillate gradually accumulated on the condenser, and the residue became more viscous. The rate of distillation was about one gram in twenty-four hours (from 8 g. of α-anhydride, and an evaporating surface of about 40 sq. cm.). The final residue when cold was very much harder and tougher than the α-anhydride. It was opaque and when heated to about 83° it suddenly became transparent but remained very stiff. At 130° it was soft enough to be drawn into continuous filaments. These filaments exhibited the phenomenon of cold drawing described in a subsequent paper.[10] The resulting fibers were lustrous and exceedingly strong and pliable, but after standing for a few days in a vacuum desiccator they became brittle and fragile. Massive specimens of the ω-anhydride also become brittle under the same conditions and lose their capacity to be drawn out into filaments. No data concerning the molecular weight of ω-polyanhydride are available, but its toughness and

[9] Carothers and Hill, paper XI.

[10] Paper XV.

viscosity indicate a considerably higher molecular weight than for the ω-polyesters described in paper XII.

The brittleness and loss of tenacity that develop when the ω-polyanhydride is stored are apparently due to hydrolysis. When a sample of the anhydride was stored at ordinary temperature in the still in which it was prepared, it retained its strength and toughness for six days. When the still was opened and the anhydride transferred to a desiccator containing anhydrous calcium chloride, brittleness developed within twenty-four hours.

The ω-anhydride adheres very firmly to the glass dish in which it is prepared, and if the specimen is more than 2 or 3 mm. deep the dish is completely shattered by the force of contraction during cooling. The ω-polyesters manifest the same behavior.

*Anal.* Calcd. for $(C_{10}H_{16}O_3)_n$: saponification equivalent, 92. Found: 92.0, 92.3.

**Sebacic β-Anhydride.**—The distillate formed from the α-anhydride during the treatment in the molecular still is a definitely macrocrystalline solid melting sharply at 68°. It dissolves readily in most of the common organic solvents with the exception of petroleum ether and ligroin. When recrystallized from a mixture of petroleum ether and benzene it separates in the form of fine needles and the melting point remains unchanged. The analytical behavior of this material identifies it as the twenty-two-membered cyclic dimer.

*Anal.* Calcd. for $(C_{10}H_{16}O_3)_n$: C, 65.18; H, 8.75; mol. wt., 368; saponification equivalent, 92. Found: C, 65.08, 64.85; H, 8.90, 8.77; mol. wt. in boiling benzene, 386, 393; saponification equivalent 91.9.

Still more decisive support for the cyclic dimeric structure for sebacic β-anhydride is found in the analysis of its behavior toward aniline when treated in the manner already described for the α-anhydride.

*Anal.* Subs. 0.939 (after treatment with aniline): 0.0992 *N* NaOH, 51.2 cc.

Thus one gram of the anhydride furnished 5.41 millimoles of hydrogen ion. The calculated value for a cyclic anhydride is 5.44, and, as the data of Table I show, this agreement demonstrates that the β-anhydride cannot be an open chain unless its molecular weight lies above 3500. But the volatility of the compound indicates that its molecular weight must lie below 1000.[11]

The neutral solution from the above titration contained both monoanilide and dianilide. The alkali used in the titration was neutralized with an equivalent amount of hydrochloric acid; the alcohol was evaporated; the residue was treated with excess hydrochloric acid to dissolve the aniline, and filtered. The residue on the filter was repeatedly extracted with boiling water until no more material dissolved. The combined filtrates on cooling deposited handsome lustrous platelets of the monoanilide, m. p. 122–123°. This compound appears not to have been described before. Recrystallization from water did not raise its melting point.

[11] Carothers, Hill, Kirby and Jacobson. THIS JOURNAL, 52, 5284 (1930).

*Anal.* Calcd. for $C_{16}H_{23}O_4N$: C, 69.26; H, 8.37. Found: C, 69.51, 69.58; H, 8.26, 8.48.

The insoluble dianilide was transferred to a Gooch crucible and weighed: yield, 0.450 g.; theory requires 0.450 g. After recrystallization from alcohol it melted at 201–202°.[12]

*Anal.* Calcd. for $C_{22}H_{28}O_2N_2$: C, 74.96; H, 8.01. Found: C, 74.49, 74.67; H, 8.34, 8.05.

The fact that dianilide was produced in this reaction demonstrates decisively that the anhydride is not monomeric, and the close agreement between the dianilide calculated and found indicates again that the structure is cyclic.

The β-anhydride is not present as such in more than traces in the α-anhydride before the molecular still treatment. The β-anhydride is exceedingly soluble in cold carbon tetrachloride, whereas rough determinations indicated that the α-compound at 25° dissolves to the extent of only about 0.04 g. in 100 cc. of carbon tetrachloride.

**Sebacic γ-Anhydride.**—When the β-anhydride is heated to its melting point, cooled and then heated again, its melting point is found to have changed from 68 to 82°. This change is due to polymerization. Samples of the new anhydride were prepared by sealing the β-anhydride in carefully dried glass tubes and heating them in a water-bath. The specimens melted at 68° to an exceedingly mobile fluid which almost instantly became so viscous that it failed to flow when the tube was inverted. When cold, the product was an opaque (or translucent) microcrystalline wax that resembled the α-anhydride. It melted at 82°, and heating at 90–100° for five hours did not raise the melting point.

When the γ-anhydride is heated in the molecular still it behaves in the same manner as the α-anhydride and is converted to the β- and ω-anhydrides.

Determinations of the molecular weight of the γ-anhydride in boiling benzene gave values in the neighborhood of 600, but for reasons already discussed in connection with the α-anhydrides we think that these values merely signify that the material is not monomeric or dimeric.

The behavior of the γ-anhydride toward aniline fails to reveal the presence of terminal carboxyl groups in detectable amounts.

*Anal.* Subs. 0.2234, 0.2707, 0.1925: (after treatment with aniline) 0.0999 *N* NaOH, 12.15, 14.70, 10.50 cc. These values correspond to 5.43, 5.43, 5.45 cc. of *N* NaOH per gram of sample.

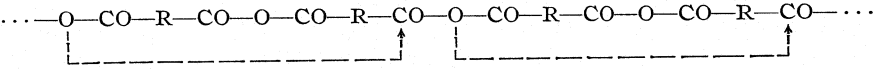
Thus one gram of the anhydride furnishes 5.44 millimoles of hydrogen ion, and from Table I it appears that if the polymer is an open chain bearing carboxyl groups at the ends, its molecular weight must lie above 7500.

[12] Pellizzari, *Gazz. chim. ital.*, **15**, 555 (1885), gives 198°; Barnicoat, *J. Chem. Soc.*, 2926 (1927), gives 200°.

## Discussion

The $\alpha$-anhydride probably bears terminal groups in the manner already indicated. We suppose that it is made up of chains of slightly differing lengths. Our idea in heating this product in the molecular still was that under these conditions it would condense or couple with itself by a process of dehydration or anhydride interchange involving the elimination of terminal groups between adjacent molecules.

A similar mechanism had already been established[13] for the transformation of the $\alpha$-polyesters into $\omega$-polyesters. The available facts are all consistent with this mechanism for the transformation of the $\alpha$-polyanhydride into the $\omega$-polyanhydride. The molecules of the latter compound therefore are very long open chains. Their molecular weights lie perhaps in the neighborhood of 30,000, certainly at not less than 15,000. The transformation of this compound into the $\beta$-anhydride evidently involves a process of anhydride interchange.




An analogous transformation occurs by heating polyesters derived from six-membered cyclic esters.[14] But among polyesters smooth depolymerization in this fashion can be effected only if the structural unit is six atoms long. Polyesters whose units are longer than six atoms yield cyclic degradation products only in small amounts and only when they are heated to a temperature sufficiently high to produce complete thermal decomposition.[15] The much smoother degradation of the anhydride is consistent with the much greater mobility and reactivity of anhydrides as compared with esters.

A peculiarity of this transformation lies in the fact that the product is not the eleven-membered cyclic monomer but the twenty-two membered cyclic dimer. A similar peculiarity exists in the nature of the cyclic degradation products from the polyesters.[15] The significance of this fact will be discussed in connection with data concerning cyclic anhydrides from other dibasic acids which will be presented in a future publication.

The formation of the $\gamma$-anhydride from the $\beta$-anhydride apparently involves merely the mutual coalescence of the cyclic molecules of the latter compound. At any rate this transformation occurs under fairly rigorously anhydrous conditions, and, since no terminal groups could be detected in the resulting $\gamma$-anhydride, one is almost impelled to conclude that the $\gamma$-anhydride is initially a very large ring. This conclusion is a little difficult to reconcile with the fact that in the molecular still the $\gamma$-anhydride

[13] Paper XII.

[14] Carothers, Dorough, and Van Natta THIS JOURNAL, **54**, 761 (1932).

[15] Carothers, *Chem. Reviews*, **8**, 381 (1931).

behaves just like the α-anhydride. According to our hypothesis the transformation of α-anhydride depends upon the presence in this compound of terminal groups capable of being eliminated by condensation between adjacent molecules. There is of course nothing theoretically to preclude the possibility of the mutual coalescence of very large anhydride rings to produce still larger rings. Moreover, it is possible that the ω-anhydride derived from the α-anhydride and that derived from the γ-anhydride are structurally different: the former may be an open chain and the latter a large ring. On the other hand, it appears that mere heating does not bring about the further polymerization of the γ-anhydride. The conditions of molecular distillation are required for this transformation. It is a little difficult to see just why the further growth of the γ-anhydride molecules, if they are rings, should occur only under conditions that favor the simultaneous elimination of smaller cyclic (β-anhydride) residues. Perhaps the resulting rupture leaves fragments (*e. g.*, bivalent radicals) that are especially prone to unite with one another.

We think it more likely, however, that traces of moisture inevitably acquired by the γ-polymer during its transfer to the molecular still may suffice to transform its molecules into open chains terminated by carboxyl groups. Coupling could then occur by the elimination of water between adjacent molecules.

One further feature of the behavior of the α-anhydride in the molecular still remains to be mentioned. It has already been indicated that degradation to the β-anhydride and growth to the ω-anhydride occur simultaneously. The latter process however reaches an apparent limit after a short time, *e. g.*, twelve hours. But this does not interrupt the formation and distillation of β-anhydride, which continues at an only slightly diminished rate until only a trace of residue remains.

## Summary

Sebacic α-anhydride formed by the action of acetyl chloride or acetic anhydride on the acid is a linear polymer. The chains are probably open and the molecular weights in the neighborhood of 5000. No smooth depolymerization of this anhydride can be effected by ordinary vacuum distillation, but in the molecular still two different transformations occur: (1) coupling of the α-anhydride with itself yields ω-anhydride, a polymer of much higher molecular weight; (2) depolymerization of the α- and ω-compounds, which occurs at the same time, yields the definitely crystalline volatile β-anhydride melting at 68°. The ω-anhydride is very tough and hard and it can be drawn out into exceedingly strong, pliable, lustrous, highly oriented fibers. The β-anhydride is a cyclic dimer (twenty-two-membered ring). When heated above its melting point it instantly polymerizes, yielding a γ-anhydride which closely resembles the α-anhydride

in its physical properties. The behavior of these anhydrides toward aniline is described and discussed. The prefixes $\alpha$, $\beta$, $\gamma$ and $\omega$ used above have been adapted arbitrarily to designate the anhydrides of different origins.

WILMINGTON, DELAWARE

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[COMMUNICATION NO. 78 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & CO.]

# STUDIES OF POLYMERIZATION AND RING FORMATION. XV. ARTIFICIAL FIBERS FROM SYNTHETIC LINEAR CONDENSATION SUPERPOLYMERS

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

RECEIVED NOVEMBER 12, 1931 PUBLISHED APRIL 6, 1932

The linear condensation superpolymers described in the three preceding papers of this series[1] can easily be drawn out into strong, pliable, transparent, permanently oriented[2] fibers. So far as we are aware no strictly synthetic material has hitherto been obtained in the form of fibers which thus simulate natural silk.

The superpolyester derived from hexadecamethylene dicarboxylic acid and trimethylene glycol is for brevity referred to below as the 3–16 $\omega$-ester.

**Methods of Producing Filaments.**—Continuous filaments can be obtained from the molten 3–16 $\omega$-ester by touching it with a stirring rod and drawing the stirring rod away. More uniform filaments are obtained by dissolving the ester in chloroform and extruding the viscous solution through an ordinary rayon spinneret into a chamber warmed to permit the evaporation of the chloroform. The filaments can be picked up and continuously collected on a motor-driven drum at the bottom of the chamber. The production of filaments having a diameter of less than 0.001 inch presents no difficulties. It is also possible to extrude the molten ester through a spinneret that is provided with a heating coil to maintain the ester in a sufficiently fluid condition. When this method is used it is easy to apply considerable tension to the filaments as they are collected on the drum.

**Properties of the Filaments.**—The properties of the filaments produced by any of these methods depend upon the amount of tension or stress applied during the spinning operation. If no stress is used the filaments closely resemble the massive ester from which they are produced. They melt at 74–75° and, like the initial mass, they are opaque and devoid of luster. But if sufficient tension is applied during the spinning operation

[1] Papers XII, XIII and XIV.

[2] The orientation implied in this use of the term is general orientation, with reference to the fiber axis, of the molecules or of some ordered units involving the molecules.

the filaments are very different from the initial mass in their physical properties. Instead of being opaque they are transparent, and they have a very high luster. They also have a very much higher breaking strength than the initial mass, and they are sufficiently pliable to be tied into hard knots, whereas the opaque filaments produced without stress are so fragile that they can hardly be bent without breaking. The opaque polyester and the transparent filaments produced from it by spinning under tension furnish very different x-ray diffraction patterns. The pattern for the opaque ester (Fig. 4) indicates that it is crystalline, but there is no sign of general orientation. The transparent filaments on the other hand furnish a fiber pattern (Fig. 5) such as one obtains from certain natural silk and cellulose fibers and rayon filaments that have been spun under tension. The character of this pattern indicates a very considerable degree of molecular orientation along the axis of the filament.[3]

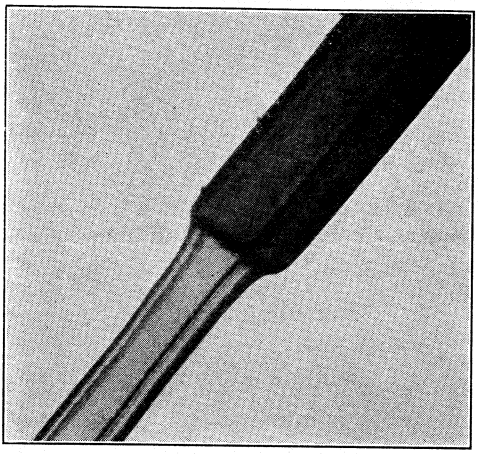


Fig. 1.—Filament from 3–16 $\omega$-ester showing opaque and transparent sections with boundary.

**Cold Drawing.**—In connection with the formation of fibers the $\omega$-polymers exhibit a rather spectacular phenomenon which we call cold drawing. If stress is gently applied to a cylindrical sample of the opaque, unoriented 3–16 $\omega$-polyester at room temperature or at a slightly elevated tempera-

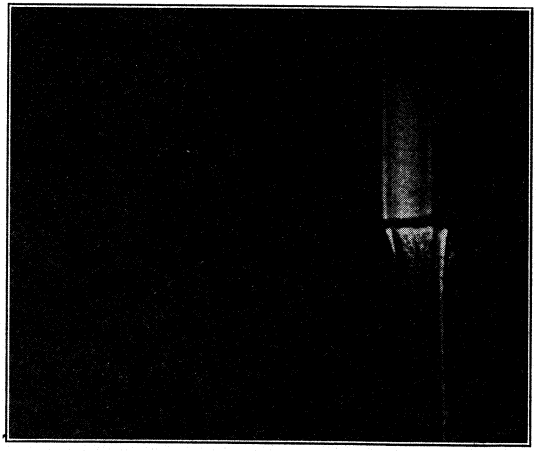


Fig. 2.—Same as Fig. 1 under crossed Nicols showing parallel extinction of oriented section.

[3] According to some preliminary calculations made by Dr. A. W. Kenney of this Laboratory, the identity periods in the oriented fibers derived from ethylene sebacate and from the 3–16 ester lie within about 10% of the calculated lengths for one structural unit of the chain.

ture, instead of breaking apart, it separates into two sections joined by a thinner section of the transparent, oriented fiber. As pulling is continued this transparent section grows at the expense of the unoriented

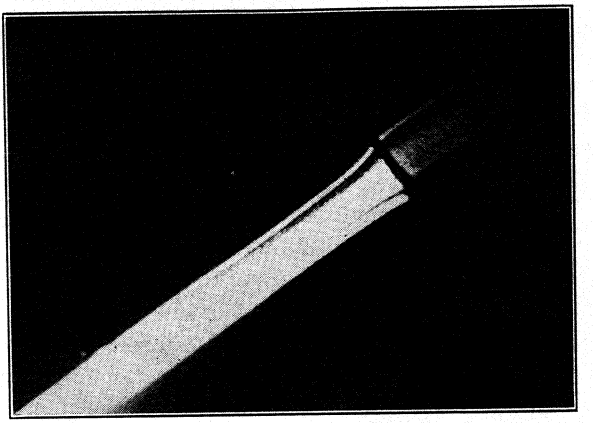


Fig. 3.—Same as Fig. 2, 45° to cross hairs.

sections until the latter are completely exhausted. A remarkable feature of this phenomenon is the sharpness of the boundary at the junction between the transparent and the opaque sections of the filament (Fig. 1).

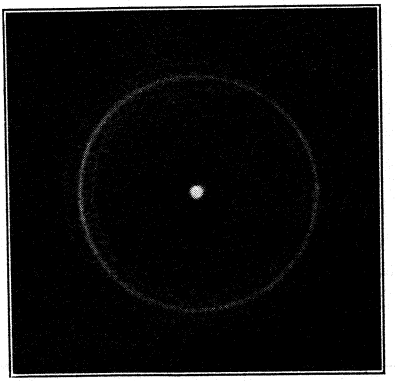


Fig. 4.—x-Ray diffraction pattern of unoriented 3–16 ω-ester.

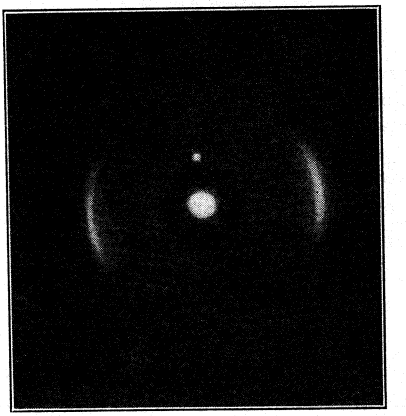


Fig. 5.—x-Ray diffraction pattern of oriented 3–16 ω-ester.

During the drawing operation the shape of this boundary does not change; it merely advances through the opaque sections until the latter are exhausted. This operation can be carried out very rapidly and smoothly, and it leads to oriented fibers of uniform cross section. The oriented and

unoriented forms of the polyester are different crystalline states, and in the cold drawing operation one crystalline form is instantly transformed into the other merely by the action of very slight mechanical stress.

Photomicrographs of filaments of the 3–16 ω-ester are reproduced in Figs. 1, 2, 3 and 6. The opaque filament shown in Fig. 1 was obtained by pulling out a specimen of the molten ester, and the transparent section attached to it was produced by cold drawing this filament. This figure shows clearly the sharpness of the boundary between the oriented and the unoriented sections. Figures 2 and 3 represent the same sample under polarized light. The oriented fiber is birefringent and shows parallel extinction. The opaque filaments of Fig. 6 were obtained by spinning a 23 weight per cent. solution in chloroform of the 3–16 ω-ester through a spinneret having 0.0045 inch holes into a chamber four feet deep heated to about 30°. At the bottom of the chamber the filaments were caught and collected on a motor driven drum. The filaments had a diameter between 0.001 and 0.002 inch. No attempt was made to stretch them during the spinning operation, and they were opaque, devoid of luster and very fragile. Nevertheless they furnished a fiber x-ray diffraction pattern practically identical with that shown in Fig. 5. Thus the x-ray data indicate a high degree of orientation while the physical properties indicate that scarcely any orientation was effected during the spinning operation. When a bundle of the filaments was warmed to about 35° and pulled it was drawn out into thin, transparent fibers which were strong and pliable. Rough determinations of the tenacity of the partially oriented opaque filaments and the oriented transparent filaments prepared from them by cold drawing indicated that the breaking strength of the transparent filaments was about six times that of the opaque filaments. This specimen of oriented fibers was used in some of the physical tests described in the next paragraph.



Fig. 6.—Filaments of 3–16 ω-ester spun from chloroform solution showing transparent fibers produced by cold drawing (× 15).

**Tenacity and Elasticity.**—Rough determinations of the tensile strength of rather thick fibers of 3–16 ω-ester prepared by pulling filaments from the molten ester and subsequently orienting them by cold drawing gave values ranging from 16 to 24 kg./sq. mm. (24,000 to 36,000 lb./sq. in. These values compare well with those for cotton fibers (*ca.* 28 kg./sq. mm.) and silk (*ca.* 35 kg./sq. mm.). Under gradually increasing stress the

fibers show a more or less definite flow point, and then, after considerable elongation, a point of increased resistance to stress. The fibers are sufficiently tough and flexible to be tied into hard knots; thick fibers are sufficiently stiff to be bristle-like.

We are indebted to Dr. W. H. Charch of the du Pont Rayon Company for a series of physical tests on fibers of the 3–16 ω-ester spun from chloroform solution and subsequently oriented by cold drawing. The observed tenacity was about 1.1 g. per denier, but this value is believed to be too low owing to the fact that no account was taken of the considerable number of broken filaments in the specimens tested. The wet tenacity is fully equal to the dry tenacity. (In the actual tests the fibers gave consistently higher values when wet than dry, but the differences probably lay within the experimental error.) A clump of filaments rolled into a small ball and compressed showed a remarkable springiness resembling wool. In their elastic properties these fibers are very much superior to any known artificial silk. In Fig. 7 are presented some slightly idealized curves taken from drawings made by a modified Richards dynamometer. Bundles of filaments of viscose rayon, natural silk and fibers from the 3–16 ω-ester were stretched for one minute and the curves show the extent and rate of recovery from stretch during the first minute after release from tension. These curves indicate that the synthetic product is even superior to natural silk, but it is possible that the silk specimen was somewhat deteriorated.

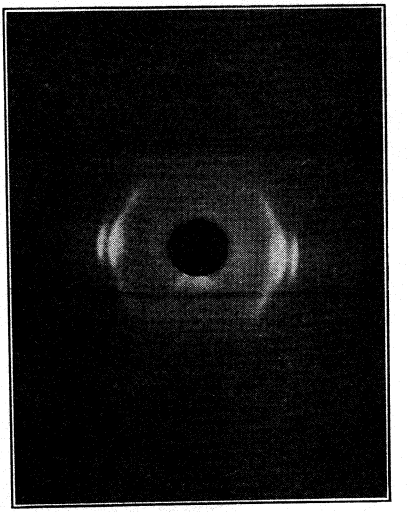


Fig. 7.—x-Ray diffraction pattern of oriented ethylene sebacate.

**Fibers from Other Linear Condensation Superpolymers.**—Fibers closely resembling those described in the preceding section have been obtained in the same way from a variety of other linear condensation polymers in the ω- or superpolymeric state. The polyesters thus far examined are those derived from ω-hydroxydecanoic acid, ω-hydroxypentadecanoic acid, ethylene glycol and sebacic acid, trimethylene glycol and adipic acid, and ethylene glycol and succinic acid. All of these materials clearly exhibit the phenomenon of cold drawing. Wide differences in the nature of the structural unit naturally have a considerable effect on the capacity to form fibers and on some of the properties of the fibers. Thus ethylene succinate in its α-form has a higher melting point and is more brittle than

most other $\alpha$-polyesters derived from dibasic acids and glycols,[4] and fibers derived from $\omega$-ethylene succinate are somewhat short and brittle. On the other hand, $\alpha$-polyesters derived from adipic acid have rather low melting points, and $\omega$-polyesters derived from the same acid show a tendency to collapse at slightly elevated temperature.

Polyamides such as that derived from $\epsilon$-aminocaproic acid can also be got in the superpolymeric state.[5] Owing to the very high polarity of the amide group and the consequent high molecular cohesion, such polyamides are exceedingly hard and insoluble in most common solvents. They show signs of melting only at temperatures sufficiently high to produce considerable decomposition. These refractory qualities make it very difficult to draw satisfactory filaments from pure polyamides. On the other hand, mixed polyester-polyamides of the type already described[5] yield filaments that are easily cold drawn and, when oriented, have very high tenacity and pliability.

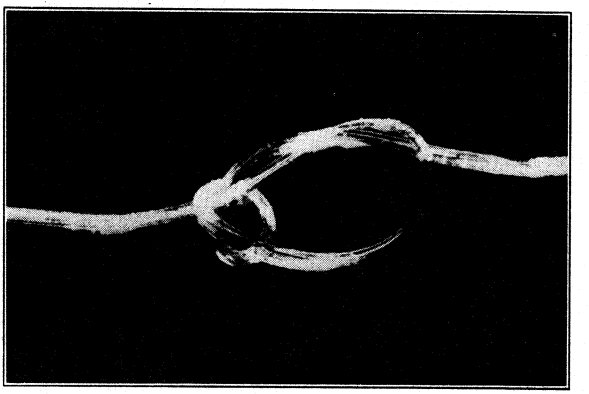


Fig. 8.—Cold drawn fiber from $\omega$-anhydride of decamethylene dicarboxylic acid. The lack of definition is due to specular reflection caused by high luster.

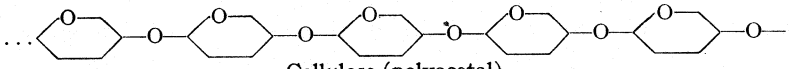
Polyanhydrides derived from dibasic acids of the series $HOOC(CH_2)_x$-COOH are especially easy to obtain in the superpolymeric state. The technique involved and the nature of the reaction is discussed in detail for sebacic acid ($x = 8$) in paper XIV. The behavior described there is characteristic (so far as the formation of superpolyanhydride is concerned) for those acids in which $x$ is greater than 4. (Actual observations thus far include those in which $x$ is 5, 6, 7, 8, 9, 10, 11, 12 and 16.) The fibers obtained from the anhydrides have an especially high degree of strength, pliability and luster (*cf.* Fig. 8) but they gradually disintegrate on standing owing to hydrolytic degradation.

[4] Carothers and Arvin, THIS JOURNAL, **51**, 2560 (1929).

[5] Paper XIII.

## Discussion

Our studies of polymerization were first initiated at a time when a great deal of scepticism prevailed concerning the possibility of applying the usually accepted ideas of structural organic chemistry to such naturally occurring materials as cellulose; and its primary object was to synthesize giant molecules of known structure by strictly rational methods. The use of synthetic models as a means of approach to this problem had already been undertaken by Staudinger, but the products studied by him (polyoxymethylene, polystyrene, polyacrylic acid, etc.) although unquestionably simpler than naturally occurring polymers, were produced by reactions of unknown mechanism, and their behavior, except in the case of polyoxymethylene, was not sufficiently simple to furnish an unequivocal demonstration of their structure. On the other hand, the development of the principles of condensation polymerization described in preceding papers of this series has led to strictly rational methods for the synthesis of linear polymers, and the structures of the superpolymers III to VI follow directly from the methods used in their preparation. Meanwhile the weight of authoritative opinion has shifted; further evidence has been accumulated,[6] and cellulose has been assigned a definite and generally accepted structure.[7] Like the synthetic products III to VI it falls in the class already defined as linear superpolymers.

I 

Cellulose (polyacetal)

II ...—NH—R—CO—NH—R′—CO—NH—R—CO—NH—R′—CO—...

Silk (polyamide)

III ...—O—R—CO—O—R—CO—O—R—CO—O—R—CO—O—R—CO—...

Polyester (from hydroxy acid)

IV ...—O—R—O—CO—R′—CO—O—R—O—CO—R′—CO—

Polyester (from dibasic acid and glycol)

V ...—O—R—CO—NH—R′—CO—NH—R′—CO—O—R—CO—...

Mixed polyester-polyamide

VI ...—O—CO—R—CO—O—CO—R—CO—O—CO—R—CO—...

Polyanhydride

Addition polymers of very high molecular weight have been synthesized in the past, but the capacity to yield permanently oriented fibers of any considerable strength has not been observed hitherto. Why is this,

[6] Haworth, Long and Plant, *J. Chem. Soc.*, **129**, 2809 (1927); Freudenberg, *Ber.*, **54**, 767 (1921); *Ann.*, **461**, 130 (1928); Freudenberg and Braun, *ibid.*, **460**, 288 (1929); Freudenberg, Kuhn, Durr, Bolz and Steinbrunn, *Ber.*, **63**, 1528 (1930).

[7] Sponsler and Dore, *Colloid Symposium Monograph*, **4**, 174 (1926). Chemical Catalog Company, New York; Sponsler, *Nature*, **125**, 633 (1930); Meyer and Mark, *Ber.*, **61**, 593 (1928); Mark and Meyer, *Z. physik. Chem.*, [B] **2**. 115 (1929); Mark and Susich, *ibid.*, **4**, 431 (1929).

and what conditions of molecular structure are requisite for the production of a useful fiber? We regret that the limitations of space prohibit a detailed discussion of these and accessory questions, and permit only the baldest statement of our conclusions.

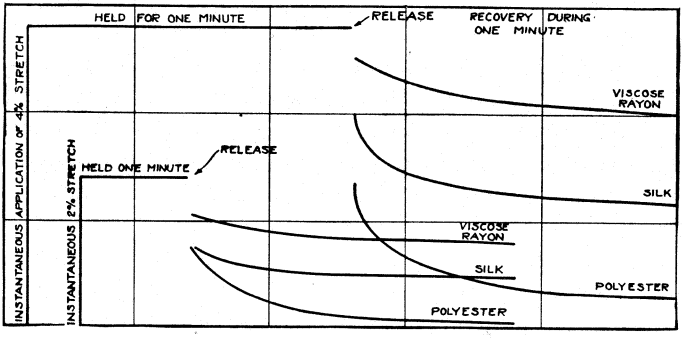



Fig. 9.—Elastic recovery of various fibers.

We picture a perfectly oriented fiber as consisting essentially of a single crystal in which the long molecules are in ordered array parallel with the fiber axis (Fig. 10). (In actual fibers a considerable number of the molecules fail to identify themselves completely with this perfectly ordered structure.) The high strength in the direction of the fiber axis and the pliability are accounted for by the high cohesive forces of the long molecules and by the absence of any crystal boundaries along the fiber axis.[7a] Fiber strength should depend upon molecular length, and recent work by Dr. Van Natta in this Laboratory indicates that it is not possible to spin continuous filaments from the polyester of hydroxydecanoic acid until its molecular weight reaches about 7000. The property of cold drawing does not appear until the molecular weight reaches about 9000. From these and other facts we conclude that a useful degree of strength and pliability in a fiber requires a molecular weight of at least 12,000 and a molecular length not less than 1000 Å. (The limits for polyamides may perhaps lie at somewhat lower values.)

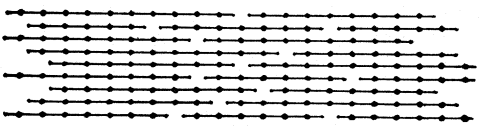


Fig. 10.—Lattice from molecules of unequal length.

Besides being composed of very long molecules, a compound must be capable of crystallizing if it is to form oriented fibers, and orientation is probably necessary for great strength and pliability. Linear condensation polymers are quite generally crystalline unless bulky substituents are

[7a] *Cf.* Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, Germany, 1930.

present to destroy the linear symmetry of the chains; addition polymers, especially those produced from vinyl compounds, are more rarely crystalline. Possible reasons for this have already been discussed in part.[8] Three dimensional polymers are obviously unsuited for fiber orientation, and synthetic materials of this class are besides invariably amorphous. Glyptal resins belong to this class.[9] It has been proposed[10] to use glyptal resins for the production of artificial silk, but our attempts to carry out the proposed process led to exceedingly fragile (though lustrous) threads which showed no signs of orientation when examined by x-rays.

Although one will not expect oriented fibers to arise by any process of spontaneous crystallization under the ordinary conditions, the phenomenon of cold drawing is perhaps only accidentally associated with the capacity to yield oriented fibers; it apparently requires a certain degree of softness and suppleness in the molecules; and its mechanism is doubtless analogous to that involved in the mechanical orientation of cellulose preparations.[11] (Perhaps however, in the unoriented polyesters the molecules are in spiral form and become extended during orientation.)

It has been suggested repeatedly by Staudinger that the great sensitivity of cellulose and rubber to degradation by heat and by certain reagents is due to the fact that the upper limit of thermal stability of the very long molecules lies close to room temperature. It is of interest in this connection that the synthetic linear superpolyesters, in spite of their very high molecular weights, are formed at 200 to 250°, and that they show no signs of being degraded by repeated exposure to elevated temperature.

## Acknowledgment

We are greatly indebted to Dr. W. H. Charch of the du Pont Rayon Company and to Dr. E. O. Kraemer of the Experimental Station for valuable criticism and advice, and we have also to thank Dr. A. W. Kenney of the Experimental Station for the x-ray data.

## Summary

The linear condensation ω-polyesters, polyanhydrides, and mixed polyester-polyamides described in preceding papers are easily drawn out into very strong, pliable, highly oriented fibers which closely simulate natural silk and cellulose fibers. These materials also resemble cellulose and silk in the essential details of their molecular structure. The significance of these analogies is discussed.

WILMINGTON, DELAWARE

[8] Carothers, *Chem. Reviews*, **8**, 415 (1931).

[9] Ref. 8, p. 402.

[10] British Patents 303,867 and 305,468.

[11] Ref. 8, p. 418.

[COMMUNICATION NO. 48 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

# STUDIES OF POLYMERIZATION AND RING FORMATION. XVI. A POLYALCOHOL FROM DECAMETHYLENE DIMAGNESIUM BROMIDE

BY WALLACE H. CAROTHERS AND JAMES E. KIRBY

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The action of bifunctional reactants on bifunctional Grignard reagents (*e. g.*, on $BrMg(CH_2)_xMgBr$) presents the possibility of producing cyclic compounds of various types. Cyclopentanone,[1] cyclohexanone and methylcyclohexanol[2] have been prepared thus, and also 5- and 6-atom rings containing phosphorus, arsenic,[3] lead[4] and silicon.[5] Concerning larger rings it is recorded[2] that diacetyl reacts with pentamethylene dimagnesium bromide but yields very little of the product corresponding in composition with the expected 7-ring glycol. The same reagent is said[6] to react with dialdehydes and diketones to give ring compounds, though "not easily;" but none of these compounds are described. The rarity and obscurity of such allusions to reactions which might yield large rings is certainly not due to any difficulty of inducing reaction between —MgX and carbonyl or other groups. On the other hand, bifunctional reactions are not obliged to choose between ring formation and frustration or abortion; they may be, and in fact when the possibility of forming a ring of 5 or 6 atoms is absent, they generally are intermolecular, and they thus lead to linear polymeric chains.[7] The diversity of the Grignard reactions should permit the preparation of linear polymers of many different types. Complications due to the usual side reactions of the —MgX group are multiplied when two of these groups are present in the same molecule. Nevertheless, as the following example shows, it is possible by such reactions to prepare linear polymers which are homogeneous in their analytical and chemical behavior.

Methyl formate (0.2 mole) was added dropwise to an ethereal solution (250 cc.) of decamethylene dimagnesium bromide prepared from 0.2 mole of the bromide. Each drop of the formate immediately yielded a heavy, voluminous precipitate. After the addition of all the formate, the mixture was refluxed for one and one-half hours. A color test[8] then showed that C—MgX was absent from the ethereal layer but present in the insoluble precipitate. The mixture was treated with water and dilute hydrochloric

[1] V. Braun and Sobecki, *Ber.*, **44**, 1918 (1911).

[2] Grignard and Vignon, *Compt. rend.*, **144**, 1358 (1907).

[3] Grüttner and Wiernik, *Ber.*, **48**, 1473 (1915).

[4] Grüttner and Krause, *ibid.*, **49**, 2666 (1916).

[5] Bygden, *ibid.*, **48**, 1236 (1915).

[6] V. Braun, *Chem. Zentr.*, II, 1993 (1909).

[7] See Carothers, THIS JOURNAL, **51**, 2548 (1929), and subsequent papers of this series.

[8] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

acid, and the undissolved solid was separated by filtration. The yield was 88% of the theoretical. The product was completely freed of magnesium by triturating it with warm dilute hydrochloric acid. It dissolved readily in hot alcohol, acetic acid, or ethylene chloride, but not in acetone, ether or benzene. It melted at about 115–120°. More sharply melting samples (*e. g.*, 120–121°) were obtained by repeated crystallization from alcohol, and higher and lower melting samples were obtained in other experiments. The melting points all varied with the rate of heating.

The analytical composition of this solid corresponds with the expected poly secondary alcohol, and its apparent molecular weight indicates an average formula $-[(CH_2)_{10}-CHOH]_5-$. The equation for the reaction may be represented as

$$\ldots-(CH_2)_{10}MgBr + O{=}C(H)-OCH_3 + BrMg-\ldots \longrightarrow \ldots-[-(CH_2)_{10}-CH(OMgBr)-]-\ldots$$

*Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.65; H, 12.94. Found: C, 77.35, 77.40; H, 13.04, 12.79. Mol. wt., calcd. for $(C_{11}H_{22}O)_5$: 850. Found (in boiling ethylene chloride): 835, 879.

It is undoubtedly mixed with traces of shorter and longer chains and with analogous derivatives of the coupling products $BrMg(CH_2)_{20}MgBr$, $BrMg(CH_2)_{30}MgBr$, etc., which are always formed in small amounts during the preparation of the reagent. The chains are probably all open, but there may be considerable variety in the nature of the terminal groups. However, its lack of homogeneity is probably no greater than that of a purified sample of polyvinyl alcohol,[9] of which it is a homolog.

The polyalcohol is readily converted into such acyl derivatives as bromobenzoyl, phthalyl, etc., but all of these products were obtained only in the form of oils or tars. The composition of an oily acetate prepared by refluxing the alcohol with acetic anhydride containing some sodium acetate confirms the empirical structure assigned to the alcohol.

*Anal.* Calcd. for $-(CH_2)_{10}-CH(OCOCH_3)- = C_{13}H_{24}O_2$: C, 73.59; H, 11.32; saponification equivalent, 212. Found: C, 74.09, 73.61; H, 11.27, 11.33: saponification equivalent, 207, 223, 227.

Experiments in other directions remain incomplete.

The behavior of the polyalcohol in the molecular still is noteworthy. A sample melting at 110–113° was heated for a few hours at about 150° under a pressure less than $10^{-5}$ mm. A trace of crystalline solid melting at about 80° collected on the condenser which was within 1 cm. of the evaporating surface. The residue was a colorless, semi-transparent, very tough pliable mass. It was insoluble in the common solvents. On being heated, it gradually became completely transparent between 60 and 100°. At 215–220° it had become somewhat soft and sticky without losing its shape. Above this temperature it first became slightly yellow and finally, at about 250°, still darker with considerable decomposition. Its analytical composition was nearly the same as that of the alcohol from which it was derived. The change in properties indicates a considerable increase in molecular weight, and the absence of solubility and complete fusibility is consistent with the development of a three-dimensional polymeric molecular structure. This might readily occur, with very little change in composition, through cross-linking of the polyalcohol chains by occasional ether formation. When the polyalcohol is heated in the same way at ordinary pressure, it remains quite unchanged in its properties; so this example provides an even more striking illustration than those

[9] Herrmann and Haehnel, *Ber.*, **60**, 1658 (1927); Staudinger, Frey and Starck, *ibid.*, **60**, 1782 (1927).

previously recorded[10] of the powerfulness of the molecular still as a tool for displacing chemical equilibria.

The description of these fragmentary experiments with bifunctional Grignard reagents is presented now because it has become necessary to suspend our work in this field.

## Summary

A crystalline polydecamethylene carbinol has been prepared by the action of decamethylene dimagnesium bromide on methyl formate. Its properties are described. It is converted into a colorless, insoluble, tough, pliable mass when it is heated in a molecular still.

[10] Papers XI, XII, XIII and XIV.

WILMINGTON, DELAWARE

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[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

# *d*-TALONIC ACID AND GAMMA-TALONOLACTONE

BY LEONARD H. CRETCHER AND ALICE G. RENFREW

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Crystalline talonic acid has been described by Hedenburg and Cretcher.[1] In common with other monocarboxylic sugar acids talonic changes slowly in aqueous solutions to an equilibrium mixture of lactone and acid. The crystalline $\gamma$-lactone was isolated for the first time during the course of this investigation.

In a study of the mutarotation of aqueous solutions of sugar acids, Levene and Sims[2] found that for several hours the change in specific rotation is determined by the dextro or levo character of the $\delta$-lactone, which forms nearly eight times as rapidly as the $\gamma$-lactone. *d*-Mannonic acid with a *cis*-configuration of the fourth and fifth hydroxyl groups gave rapidly increasing dextro readings during the first four hours, and subsequently showed a slow rise in dextro values. In the case of sugar acids which have the $\gamma$- and $\delta$-hydroxyl groups in *trans* positions, Levene and Sims[2] and Rehorst[3] have observed that the values for specific rotation pass through an early maximum or minimum, corresponding to the formation of $\delta$-lactone.

As Rehorst has noted—in accordance with Hudson's rule and in analogy with the behavior of similarly constituted acids—*d*-talonic acid solutions might be expected to give a series of increasing dextro readings[4] before

[1] Hedenburg and Cretcher, THIS JOURNAL, **49**, 478 (1927).

[2] Levene and Sims, *J. Biol. Chem.*, **65**, 31 (1925).

[3] Rehorst, *Ber.*, **63**, 2279 (1930).

[4] Freudenberg and Kuhn have questioned the validity of a generalization based on these premises and have presented an extensive analysis of rotational data [Freudenberg and Kuhn, *Ber.*, **64**, 703 (1931)].

the more levo readings characteristic of the formation of γ-lactone become apparent. For most of the solutions of talonic acid studied polarimetrically, a slight increase in dextrorotation was observed. Invariably for an interval of thirty to forty-five minutes no decrease in dextrorotation was observed; the decrease, once apparent, became a constant change. The initial lag, including a slight upward trend, definitely suggests the formation of a dextrorotatory δ-lactone. However, if this lactone forms, it must be present in small quantity or must have a specific rotation little higher than the free acid. Talonic acid prepared by alkaline hydrolysis of the pure γ-lactone and liberation of the hexonic acid with hydrochloric acid gave readings which corresponded closely to the values obtained for the crystalline acid, and showed a small dextro mutarotation during the first half-hour.

It is especially worth noting that although freshly prepared solutions of talonic acid give no evidence of γ-lactone when titrated with $N/10$ sodium hydroxide, nearly 4% of lactone was determined by titration after one hour; during this interval no comparable decrease in specific rotation was recorded. As shown in Table I, the percentages of γ-lactone calculated from titration values are definitely higher than the percentages calculated from the polarimetric readings of the same solutions during the first twenty-four hours. Such a difference in apparent percentages of γ-lactone is similar in character to the differences observed by Levene and Sims[2] for gulonic acid. The rate of formation of γ-talonolactone is of approximately the same order as the rate for γ-galactonolactone.[2]

TABLE I

CRYSTALLINE TALONIC ACID—LACTONE FORMATION

| Time | $[\alpha]_D$ | $(M)/100$ | *A* % γ-lactone calcd. from optical rotation | *B* % γ-lactone detd. by titration |
|---|---|---|---|---|
| 3 min. | +18.24° | +37.4° | | |
| 1 hour | +18.13 | +37.2 | 0.2 | 4.8 |
| 2 hours | +17.86 | +36.6 | 0.9 | 6.1 |
| 5 hours | +16.74 | +34.3 | 3.1 | 9.0 |
| 7.5 hours | +15.18 | +31.1 | 6.3 | 12.3 |
| 24 hours | +10.16 | +20.8 | 16.7 | 19.6 |
| 55 hours | + 1.33 | + 2.6 | 35.0 | 34.7 |
| Pure lactone | −34.7 | −61.7 | | |

## Experimental

***d*-Talonic Acid.**—Talonic acid was prepared according to the method of Hedenburg and Cretcher[1] by the epimerization of galactonic acid with pyridine at 90–100°. The aqueous solution of the free acid, obtained by decomposition of the cadmium salt, was rapidly concentrated *in vacuo*. In one case the solid product began to separate from the solution before the distillation was discontinued; this product and the further concentrated mother liquor were treated with a large volume of absolute alcohol and chilled several hours before filtration. The crude talonic acid (m. p. 122–125°) was recrystal-

lized from absolute alcohol, in which it is difficultly soluble. The melting point of the recrystallized acid was 138°, and a freshly prepared 4% aqueous solution was strongly dextrorotatory as previously reported.[1] Different preparations gave $[\alpha]_D^{25}$ +18.97°, +18.24°, +19.35°, +19.65°. Talonic acid as liberated from the sodium salt had a correspondingly high specific rotation. The crystalline substance titrated as a free acid with one-half molecule of water of crystallization.

Table II gives typical readings for a solution of talonic acid. Obviously the observed increase in dextro rotation was very small, but the change was noted with most solutions by several investigators in this Laboratory. The temperature was maintained at 25° for two or more hours. As mixtures of talonic acid and lactone approach an equilibrium ratio, the specific rotation changes very slowly. It was hoped that the initial changes in the rotation of talonic acid solutions would be accentuated by conditions which might decrease the reaction velocity. However, measurements made at 9° and a study of a solution of the acid in 50% alcohol gave similar but not more striking variations.

TABLE II

MUTAROTATION DATA

| Hours | Crystalline acid $[\alpha]$ $l = 4$; $c = 4.4804$ | $[\alpha]$ |
|---|---|---|
| 0.05 | +3.27° | +18.24° |
| .083 | 3.27 | 18.24 |
| .10 | 3.29 | 18.35 |
| .25 | 3.30 | 18.40 |
| .41 | 3.29 | 18.35 |
| 1.0 | 3.25 | 18.13 |

At intervals 2-cc. samples of the solution used for polarimetric study were titrated with $N/10$ sodium hydroxide. The specific rotations calculated for titrated solutions of acid and lactone are in all cases of a lower dextro value than the rotations actually observed. Such a deviation points to the presence of an additional dextrorotating component. Table III gives characteristic observed and calculated specific rotations, as well as the equilibrium values reached by talonic acid solutions. Similar data was obtained for other talonic acid solutions.

TABLE III

DEVIATION OF OBSERVED AND CALCULATED SPECIFIC ROTATIONS

| Time | γ-lactone by titration | $[\alpha]$ Observed | $[\alpha]$ Calcd. from titration data | Deviation in $[\alpha]$ |
|---|---|---|---|---|
| 1 hour | 4.8% | +18.13° | +15.7° | 2.4° |
| 2 hours | 6.1 | +17.86 | +14.0 | 3.8 |
| 7.5 hours | 12.3 | +15.2 | +11.7 | 3.5 |
| 55 hours | 34.7 | + 1.33 | − 0.1 | 1.4 |
| 16 days | 75.5 | −21.1 | −21.7 | 0.6 |
| Soln. heated | 81.4 | −24.0 | −24.8 | 0.8 |

**Preparation of γ-*d*-Talonolactone.**—It was found that fairly pure γ-lactone could be obtained from very concentrated aqueous sirups of approximately equilibrium mixtures of talonic acid and lactone, when crystallization had been started by mechanical agitation or by seeding. The lactone crystallized from the concentrate of talonic acid solutions which had been heated several hours at 100° or four hours at 60–75°. A small amount of insoluble amorphous material formed during prolonged heating. If the sirups were seeded and allowed to stand for several days, the large hard crystals could be readily freed from the mother liquor by filtration and careful washing with 70–80% alcohol. In one case the lactone crystallized in transparent prisms from a dilute solution during the reconcentration of the alcoholic mother liquors from the preparation of talonic acid.

The lactone was recrystallized from water and from 75% alcohol. Final recrystallization from glacial acetic acid, from absolute alcohol or from water gave material melting at 132–134°. Water is not a convenient medium for recrystallization, because the solutions must be very concentrated before the lactone can be recovered.

*Anal.* Calcd. for $C_6H_{10}O_6$: C, 40.45, H, 5.66. Found: C, 40.44; H, 5.69.

The γ-lactone is quite stable in aqueous solutions, $[\alpha]_D^{25}$ −34.65°; $\alpha$ = −1.66°; $l$ = 2; $c$ = 2.3951 g. No change in rotation was observed in two hours; after six hours $[\alpha]$ = −34.0°; after twenty-four hours $[\alpha]$ = −33.5°; and after five days $[\alpha]$ = −28.4°. A solution of lactone, which had been heated for several hours at 100°, to apparent equilibrium, had a specific rotation of $[\alpha]$ = −28.7° and titrated for 11% of free acid. Although the ratio of free acid and lactone was not the equilibrium value reached by solutions of the crystalline acid, it seems probable that the difference was due to the extremely slow rate of change of solutions in this general range of concentration. Several prepared solutions of acid–lactone mixtures, containing between 11 and 18% molar proportions of crystalline acid, showed no deviation from the calculated specific rotation. These solutions changed very slowly in the direction of higher acid concentration.

The titration of a solution of talonolactone (well cooled in ice water) gave no evidence of free acid. The complete neutralization of the lactone was accomplished after heating above room temperature.

*Anal.* 0.1197 g. of lactone required 6.74 cc. of *N*/10 NaOH (phenolphthalein). Calcd. for $C_6H_{10}O_6$: 6.73 cc.

Classification as a γ-lactone is based on the slow change in the specific rotation of aqueous solutions,[5] the levorotation of such solutions (Hudson's rule), and the delayed neutralization of dilute alkali.

A sample of talonic lactone was hydrolyzed with normal sodium hydroxide, and free talonic acid liberated with normal hydrochloric acid.[2] 0.9148 g. of lactone in 25 cc. is equivalent to 1.0535 g. of acid: four minutes after the addition of hydrochloric acid, $[\alpha]_D^{25}$ +18.50°; $\alpha$ = +3.12°; $l$ = 4; $c$ = 4.214 g. The agreement in specific rotation with the values determined for solutions of the crystalline acid affords a cross-check on the purity of the two preparations. The initial dextro mutaroration of such solutions was of the same order as that observed for the crystalline acid.

## Summary

1. The determination of the specific rotation of *d*-talonic acid has been repeated. The values obtained for the crystalline acid and for the acid liberated from the sodium salt are slightly higher than the specific rotation reported by Hedenburg and Cretcher.

[5] Haworth, "The Constitution of Sugars," Edward Arnold & Co., 1929, p. 14.

2. The shape of the mutarotation curve for talonic acid solutions is indicative of the formation of a dextro rotating $\delta$-talonolactone, as well as a levo rotating $\gamma$-talonolactone.

3. $\gamma$-Talonolactone has been separated in crystalline form.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# THE REACTION BETWEEN ORGANIC MAGNESIUM HALIDES AND ALPHA-BROMO KETONES

BY E. P. KOHLER AND M. TISHLER

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Many years ago Kohler and Johnstin[1] studied the action of organic magnesium halides on $\alpha$-bromo-$\beta,\beta$-diphenyl propiophenone and, for reasons which seemed good at the time, represented the process with the equation

$$(C_6H_5)_2CHCHBrCOC_6H_5 + 2RMgBr = (C_6H_5)_2CHCH{=}C\begin{matrix}OMgBr\\C_6H_5\end{matrix} + R{\cdot}R + MgBr_2$$

A few years later Umnowa[2] treated $\alpha$-bromo-pentamethyl acetone with methylmagnesium iodide and obtained a similar result, but, for reasons which likewise seemed good at the time, represented the process in a different manner

$$(CH_3)_3CCOCBr(CH_3)_2 + CH_3MgI = (CH_3)_3CCOC(CH_3)_2 + CH_3Br$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad MgI$$

Quite recently Löwenbein and Schuster[3] rediscovered the reaction, represented their product with a formula similar to the one adopted by Kohler and Johnstin and proposed a mechanism which, in the case studied by them, was plausible

$$(C_6H_5)_2\underset{\text{I}}{C}BrCOC_6H_5 + C_6H_5MgBr \longrightarrow MgBr_2 + C_6H_5(C_6H_5{-}C_6H_5) +$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$(C_6H_5)_2C{-}COC_6H_5 \rightleftharpoons (C_6H_5)_2C{=}\underset{\text{II}}{C}C_6H_5 + C_6H_5MgBr \longrightarrow$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OMgBr$$
$$(C_6H_5)_2C{=}CC_6H_5 + C_6H_5(C_6H_5{-}C_6H_5)$$

Fisher, Oakwood and Fuson,[4] who came across the same reaction when they treated tribromoacetomesitylene with alkyl magnesium halides, likewise preferred to represent their magnesium derivative as an enolate.

[1] Kohler and Johnstin, *Am. Chem. J.*, **33**, 45 (1905).

[2] Umnowa, *Chem. Zentr.*, **84**, I, 1402 (1913); *J. Russ. Phys.-Chem. Soc.*, **45**, 881 (1913).

[3] Löwenbein and Schuster, *Ann.*, **481**, 106 (1930).

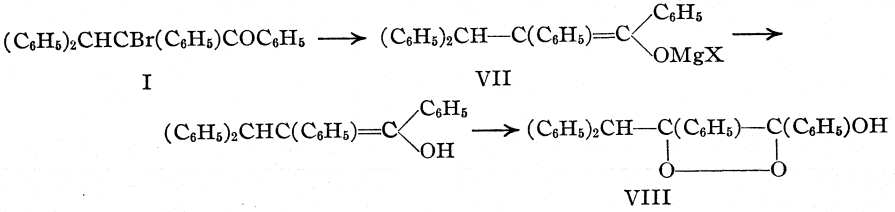
[4] Fisher, Oakwood and Fuson, THIS JOURNAL, **52**, 5038 (1930).

Meanwhile, however, Kohler, Richtmyer and Hester,[5] having occasion to employ the reaction for the preparation of a sensitive bromohydrin, examined it quantitatively and found that per mole of bromo compound only one mole of the organic magnesium halide disappears. Accordingly neither Kohler and Johnstin's equation nor Löwenbein and Schuster's mechanism can be correct, even though the latter report that they isolated exactly one mole of diphenyl.

In view of these discrepancies we decided to subject the reaction to a more careful investigation in which both the structure of the resulting magnesium compound and the fate of the hydrocarbon residue in the organic magnesium halide were to be established. Quantitative determinations made with a series of α-bromo or α-iodo ketones showed that the course of the reaction is always the same, as can be seen from the results presented in the following table in which the substances listed as "products" are the compounds obtained after decomposition with water and acid. The reagent in every case was methylmagnesium iodide.

| | Substances | Moles of reagent | Products |
|---|---|---|---|
| I | $(C_6H_5)_2CHC(C_6H_5)BrCOC_6H_5$ | 1 | $(C_6H_5)_2CHCH(C_6H_5)COC_6H_5$ |
| II | $(C_6H_5)_2CHCHBrCOC_6H_5$ | 1 | $(C_6H_5)_2CHCH_2COC_6H_5$ |
| III | $(C_6H_5)_2CHCHICOC_6H_5$ | 1 | $(C_6H_5)_2CHCH_2COC_6H_5$ |
| IV | $(C_6H_5)_2CBrCOC_6H_5$ | 1 | $(C_6H_5)_2CHCOC_6H_5$ |
| V | $C_6H_5COCHBrCOC_6H_5$ | 2 | $C_6H_5COCH_2C(C_6H_5)(CH_3)OH$ |
| VI | $C_6H_5COCBr_2COC_6H_5$ | 2 | $C_6H_5COCHBrC(C_6H_5)(CH_3)OH$ |

For the purpose of establishing the structure of the resulting magnesium compound, we employed the reaction between phenylmagnesium bromide and α-bromo-triphenyl-propiophenone (I). Here the product is a colorless crystalline magnesium compound. On decomposition with iced acid in the presence of ether, this magnesium compound gave a solution which absorbed oxygen from the air, forming a peroxide of known structure.[6] The magnesium derivative is therefore an enolate.



For the purpose of establishing the fate of the hydrocarbon residue in the halide, we employed the reaction between α-iododiphenylpropiophenone and phenylmagnesium bromide. It yielded, in addition to the corresponding magnesium enolate, a liquid which was identified as iodo-

[5] Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 205 (1931).

[6] Kohler, *Am. Chem. J.*, **36**, 189 (1906).

benzene by analysis and by conversion into phenyliodochloride. Diphenyl was also found, but only in the amount to be expected in the quantity of phenylmagnesium bromide used. The reaction must, therefore, be represented by the equation

$$\underset{\text{III}}{(C_6H_5)_2CHCHICOC_6H_5} + C_6H_5MgBr = \underset{\text{IX}}{(C_6H_5)_2CH{-}CH{=}C(OMgBr)C_6H_5} + C_6H_5I$$

Umnowa based her interpretation of the reaction on the fact that her magnesium derivative, corresponding to VII and IX, combined with carbon dioxide to form a salt of a carboxylic acid. Her facts are, doubtless, correct, but her conclusions are no longer valid. It is known, now, that sodium enolates readily combine with carbon dioxide, and that the products are salts of carboxylic acids.[7] Carbonation, therefore, can no longer be regarded as a reliable method for establishing the structure of metallic derivatives. Our magnesium derivatives likewise combine with carbon dioxide; in the case of the enolate represented by IX it was possible to establish the structure of the resulting acid by esterifying it and then synthesizing the same ester by a method that leaves no doubt as to its structure.

$$\underset{\text{IX}}{(C_6H_5)_2CHCH{=}C(OMgX)C_6H_5} \longrightarrow \underset{\text{X}}{(C_6H_5)_2CH{-}\underset{\displaystyle COOH}{\underset{|}{C}}HCOC_6H_5} \longrightarrow \underset{\text{XI}}{(C_6H_5)_2CH\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}HCOC_6H_5}$$

$$C_6H_5COCH_2COOC_2H_5 + (C_6H_5)_2CHBr + NaOC_2H_5 \longrightarrow \underset{\text{XI}}{(C_6H_5)_2CH\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}HCOC_6H_5}$$

By benzoylating this same magnesium compound Kohler and Johnstin formed a product which had previously been obtained in a different manner and which had been formulated as a benzoate.[8]

$$C_6H_5CH{=}CHCOC_6H_5 \longrightarrow (C_6H_5)_2CHCH{=}C(OMgX)C_6H_5 \longrightarrow \underset{\text{XII}}{(C_6H_5)_2CHCH{=}C(OCOC_6H_5)C_6H_5}$$

$$\underset{\text{XIII}}{(C_6H_5)_2CH{-}CH(COC_6H_5)_2}$$

The evidence on which formula XII was preferred to formula XIII likewise is no longer valid, it being known, now, that alkylated diketones are cleaved at least as easily as esters of the type represented by XII are hydrolyzed, and also that alkylation depresses the enolization or reduces the acidity of diketones to such a degree that they no longer form copper derivatives when shaken with copper acetate. In order to decide this

[7] Brühl, *Ber.*, **24**, 3387 (1891); Schlenk, Hillemann and Rodloff, *Ann.*, **487**, 135 (1931).

[8] Kohler, *Am. Chem. J.*, **31**, 642 (1904).

matter we synthesized the diketone XIII by a method analogous to that employed in the synthesis of the ester XI.

$$C_6H_5COCH_2COC_6H_5 + (C_6H_5)_2CHBr + NaOC_2H_5 \longrightarrow (C_6H_5)_2CHCH(COC_6H_5)_2$$

The diketone obtained in this manner and the benzoylation product proved to be the same substance; the latter is therefore not the benzoate XII but the diketone XIII.

The mechanism by which these magnesium enolates yield products which are to some extent like those obtained from Grignard reagents need not be discussed here; it is doubtless the same as that by which the corresponding sodium enolates of Schlenk form similar products. Discussion of the mechanism by which the enolates are formed can likewise be deferred until the limits of the reaction have been explored more thoroughly. It is clear, already, that the reaction is far from general and that the outcome depends not only upon the complexity of the ketone, but also, to a surprising degree, upon the chemical character of the reagent.

## Experimental Part

**Reaction with α-Bromo-α,β,β-triphenyl-propiophenone, I.**—Twenty grams of the finely powdered ketone was added, gradually, to a chilled solution of phenylmagnesium bromide which had been prepared from 1.25 g. of magnesium. The clear liquid was boiled for fifteen minutes—during which time it deposited a solid magnesium derivative—then cautiously poured into a freezing mixture of ice and hydrochloric acid. The ethereal layer was washed rapidly with water and divided into two portions of which one was exposed to a strong draft in an evaporating dish and the other evaporated in a rapid current of air while it was cooled in a freezing mixture. Both portions left an oily residue.

The oil was dissolved in a minimum quantity of acetone. The resulting solution was diluted with low boiling petroleum ether, freed from suspended water by shaking with calcium chloride and cooled. It first deposited a small quantity of triphenylpropiophenone, and then a mixture which melted at 112–114°. After repeated recrystallization from acetone and petroleum ether, this mixture yielded a pure compound which crystallized in small lustrous prisms, melted at about 126°, and had all the characteristic properties of the peroxide represented by VIII. Thus when 5 g. of the substance was heated in a large flask, it decomposed in a series of slight explosions, the products being 3.1 g. of diphenylacetophenone and 1.1 g. of benzoic acid. The same products were obtained also when the substance was digested with alcoholic potassium hydroxide

$$(C_6H_5)_2CH{-}C(C_6H_5)(O{-}O){-}CC_6H_5 \longrightarrow (C_6H_5)_2CH{-}COC_6H_5 + C_6H_5COOH$$

**Reaction with Bromodibenzoylmethane. V.**—It has recently been shown that dibenzoylmethane reacts with two moles of a Grignard reagent, forming in succession a mono and a dimagnesium derivative.[9] Bromodibenzoylmethane reacts in precisely the same manner, consuming the same amount of reagent and forming the same two magnesium derivatives

$$C_6H_5COCHBrCOC_6H_5 \longrightarrow \underset{\text{A}}{C_6H_5C(OMgBr){=}CHCOC_6H_5} \longrightarrow \underset{\text{B}}{C_6H_5C(OMgBr){=}CHC(OMgBr)(C_6H_5)_2}$$

[9] Kohler and Erickson, THIS JOURNAL, 53, 2301 (1931).

Thus when a solution of phenylmagnesium bromide prepared from 1 g. of magnesium was added to an ethereal solution of 12.5 g. of the bromo ketone the result was a soluble magnesium derivative which when manipulated in the usual manner yielded 9 g. of dibenzoylmethane. And when, operating in the usual manner, the same quantity of bromo ketone was added to a solution of phenylmagnesium bromide prepared from 2.5 g. of magnesium, the result was a solid magnesium compound which yielded 10.5 g. of β-hydroxy-β,β-diphenylpropiophenone.

**α-Iodo-β,β-diphenylpropiophenone. III.**—The iodo ketone can be prepared by heating the corresponding bromo compound with potassium iodide in methyl alcohol, but the operation is troublesome and the yield is small. At the boiling point of methyl alcohol the reaction is too slow to be of any service. It is slow even at 100°; after the mixture had been heated at this temperature for fifty hours, the yield of impure iodo compound did not exceed 50%.

It is relatively easy, however, to transform the bromo into the iodo compound by way of the magnesium derivative. Thus 18.2 g. of the solid bromo ketone was added in the course of ten minutes to a solution of phenylmagnesium bromide which had been prepared from 1.33 g. of magnesium. The mixture was boiled for an hour, then treated while hot with 12.7 g. of iodine. The boiling was continued for another hour, during which the liquid deposited a quantity of brown solid. On decomposition with ice and dilute sulfuric acid the mixture deposited most of the iodo ketone as a finely divided crystalline solid. The solid was washed with water and thiosulfate, dried and recrystallized from benzene. The ethereal filtrate contained 1.9 g. of the same material. The yield was 19.4 g. or 94%.

*Anal.* Calcd. for $C_{21}H_{17}IO$: C, 61.3; H, 4.2. Found: C, 61.4; H, 4.4.

The iodo compound is very sparingly soluble in alcohol, in ether, and in cold benzene, moderately soluble in hot benzene. From its solution in boiling benzene it separates, on cooling, as a flaky white powder which melts with decomposition at 184–185°.

**Reaction with Phenylmagnesium Bromide.**—A solution of phenylmagnesium bromide was prepared from 39 g. of bromobenzene and, in order to remove the halide as completely as possible, a large excess of magnesium. The solution was filtered and chilled in ice water. To the cold solution 41.2 g. of the solid iodo ketone was added in small quantities with constant stirring. The mixture was stirred for an hour and a half, then boiled for half an hour and after that decomposed with iced hydrochloric acid. The washed and concentrated ethereal solution deposited 27 g. of β,β-diphenylpropiophenone, which was identified by comparison with a sample on hand. The yield was 94%.

The ethereal filtrate from the ketone, when freed from ether, left an oily residue which was distilled with steam. A small quantity of diphenyl solidified in the cold condenser, but most of the material collected as a heavy liquid in the receiver. The distillate was extracted with ether and the ethereal solution was dried and distilled. It yielded 18 g. of a colorless liquid which distilled completely between 184 and 190°. In a halogen determination 0.2200 g. of this liquid gave 0.2445 g. of a silver halide which was converted into 0.1484 g. of silver chloride. The silver halide was therefore pure silver iodide and the liquid from which it was obtained must contain at least 96.5% of iodobenzene. Assuming that diphenyl is the only impurity, the quantity contained in the liquid cannot exceed 0.7 g. and the maximum amount recovered from the reaction must be under 1 g.—approximately the quantity to be expected in the reagent.

**Conversion into Phenyliodochloride.**—In order to complete the identification of the iodobenzene, chlorine was passed into a solution of 5.2 g. of the liquid in 20 cc. of chloroform. A solid began to separate almost immediately and in a short time the

solution deposited 6.6 g. of the characteristic yellow needles of the iodochloride—a yield of 93.6%.

**Action of Carbon Dioxide on the Enolate.**—Sixteen grams of solid α-bromo-β,β-diphenylpropiophenone was added in the course of ten minutes to a solution of phenylmagnesium bromide prepared from 1.2 g. of magnesium. The mixture was boiled for an hour, then chilled to 3°. Carbon dioxide was passed into the cooled liquid for five hours and then another hour at the ordinary temperature. A gummy precipitate formed at first, but the gum gradually changed to an amorphous white solid. The solid was collected on a filter in order to be able to decompose the solid and the ethereal solution separately. The ethereal filtrate, on acidification, gave 0.5 g. of unchanged bromo ketone and a small quantity of acid.

The solid was decomposed by prolonged shaking with ether and dilute sulfuric acid. The ethereal layer contained 10.6 g. of an acid—removed by extraction with sodium carbonate—and 2.5 g. of β,β-diphenylpropiophenone which may have been formed by loss of carbon dioxide from the acid. The acid was purified by recrystallization from acetone and petroleum ether.

*Anal.* Calcd. for $C_{22}H_{18}O_3$: C, 79.9; H, 5.5. Found: C, 79.8; H, 5.6.

**Diphenylmethylbenzoylacetic Acid (X).**—The acid is readily soluble in all common organic solvents except petroleum ether. It crystallizes in small colorless needles and melts with brisk evolution of carbon dioxide at 134°.

**Esterification.**—An attempt to esterify the ketonic acid by converting it into the sodium salt and treating a solution of the salt with diethyl sulfate was unsuccessful—the acid lost carbon dioxide and the product was the ketone. Esterification through the silver salt proved more successful.

A suspension of the salt—which had been thoroughly dried in a vacuum desiccator—in absolute ether, was boiled with excess of ethyl iodide for half an hour, during which the voluminous silver salt changed to silver iodide. After filtration, the ethereal solution was evaporated. It left an oil that solidified on cooling. The solid was purified by recrystallization from alcohol.

*Anal.* Calcd. for $C_{24}H_{22}O_3$: C, 80.4; H, 6.2. Found: C, 80.2; H, 6.4.

**Ethyl Diphenylmethylbenzoyl Acetate. XI.**—The ester is readily soluble in acetone, moderately soluble in ether and in boiling alcohol, sparingly soluble in cold alcohol. It crystallizes in very fine needles and melts at 135–136°.

**Synthesis of the Ester.**—To a solution of 0.6 g. of sodium in 25 cc. of absolute alcohol were added first, 5 g. of benzoyl acetic ester and then little by little, 6.5 g. of diphenylmethyl bromide. The solution gradually lost its yellow color, became cloudy, and in the course of half an hour solidified completely. The solid was collected on a filter and washed with a little alcohol, then dissolved in ether. The washed and dried ethereal solution, on concentration, deposited 5 g. of a crude product that melted at 129–133° and one gram more of the same product was obtained by suitable manipulation of the alcoholic filtrate. After recrystallization from absolute alcohol the melting point was 135–136°. The melting point of a mixture of this ester and the one obtained in the preceding experiment was 134–136°.

**Synthesis of Diphenylmethyldibenzoylmethane. XIII.**—To a solution of 0.5 g. of sodium in 25 cc. of absolute alcohol were added in succession 5 g. of dibenzoylmethane and 6.5 g. of diphenylmethyl bromide. Owing to the sparing solubility of the sodium derivative of the diketone, the conditions were not as favorable as in the synthesis of the ketonic ester, but the reaction yielded 1.4 g. of a product which even when crude melted at 217–220° and which was readily identified with the product obtained by treating the magnesium enolate IX with benzoyl chloride.

## Summary

The reaction between an organic magnesium halide and an α-bromo ketone, in which the carbonyl group is relatively inactive, is represented by the equation

$$RCHBrCOR + R_1MgBr = RCH{=}C(OMgBr)R + R_1Br$$



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[CONTRIBUTION FROM THE INSECTICIDE DIVISON, BUREAU OF CHEMISTRY AND SOILS]


# TOXICAROL. III. A RELATION BETWEEN TOXICAROL AND THE ROTENONE GROUP OF FISH POISONS


BY E. P. CLARK



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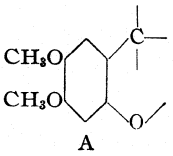
It has been shown[1] that rotenone, deguelin and tephrosin are structurally related in that, among other things, all three compounds possess the atomic grouping represented by formula A.



A

As toxicarol, the other member of this group of fish poisons, is characterized by properties so similar to those possessed by the first three, it has been assumed that, in all probability, this substance has some structure common to the others. Proof of this assumption has recently been obtained as a result of a series of experiments which are described in what follows.

Permanganate oxidation of dehydrotoxicarol in acetone has yielded risic and 2-hydroxy-4,5-dimethoxybenzoic acids. In this reaction the yield of the benzoic acid was essentially the same as that obtained from dehydrodeguelin,[1] but the risic acid, although always present, was obtained in small and variable quantities.

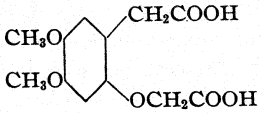
When dehydrotoxicarol was boiled gently with an alcoholic potassium hydroxide solution, the material formed an acid apparently analogous to deguelic[2] and derrisic[3] acids, although it was impossible to obtain it in a crystalline condition. However, when the acidic material was separated from the reaction mixture, dissolved in aqueous alkali, and oxidized with potassium permanganate, risic acid was obtained. If, instead of potassium permanganate, hydrogen peroxide was used as an oxidizing agent, a good yield of derric acid was obtained. These products are the same as those formed under identical conditions with deguelic and derrisic acids, derived, respectively, from deguelin and rotenone.

[1] Clark, THIS JOURNAL, **53**, 3431 (1931).

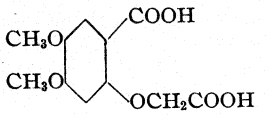
[2] Clark, *ibid.*, **53**, 316 (1931).

[3] Butenandt and Hildebrandt, *Ann.*, **477**, 249 (1930).

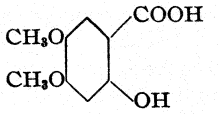
Recently LaForge[4] has presented evidence to show that derric and risic acids have respectively the structures represented by the formulas B and C. For comparative purposes the formula for 2-hydroxy-4,5-dimethoxybenzoic acid, D, is also given.




B. Derric acid




C. Risic acid




D. 2-Hydroxy-4,5-dimethoxybenzoic acid

It thus follows that toxicarol has the same atomic grouping represented by formula A, as have rotenone, deguelin and tephrosin. As the products B, C and D are obtained in a similar manner from all four substances, it is possible that the skeletons in each, immediately adjacent to the methoxylated benzene ring, which gives rise to the side chains in the three acids, are in each case essentially the same, but with the information at present available concerning this point, it is considered unjustifiable to postulate any further statement than that which is given above.

## Experimental

**Permanganate Oxidation of Dehydrotoxicarol.**—A mechanically stirred suspension of 5 g. of dehydrotoxicarol in 350 cc. of acetone, cooled to 0°, was oxidized with 18 g. of potassium permanganate. The reagent was added in 2-g. portions from time to time as the acetone became colorless. When the specified quantity of permanganate had been added and the reaction was completed, the manganese dioxide was removed by filtration and thoroughly extracted with boiling water. The aqueous extract was filtered, acidified to Congo red with sulfuric acid and concentrated under reduced pressure to approximately 100 cc. The concentrate was allowed to stand overnight for the 2-hydroxy-4,5-dimethoxybenzoic acid to separate. The yield was 0.7 g. When the experiment was repeated 1 g. of the product was obtained.

The crude acid was purified by boiling a slightly alkaline 1% solution of its potassium salt with hydrogen peroxide until most of the dark color was discharged, after which the liquid was acidified with acetic acid and filtered through norit. The filtrate was then heated to boiling, and the pure acid was separated by adding dilute sulfuric acid to the clear solution. It crystallized as colorless and, for the most part, twinned plates which melted with decomposition at 210°. When it was mixed with an authentic sample of 2-hydroxy-4,5-dimethoxybenzoic acid, no depression of the melting point occurred. It also gave a deep blue color with ferric chloride.

The mother liquors from the crude acid just described contained risic acid which was separated by extracting the liquid with ether. The yield of the crude acid from 5 g. of dehydrotoxicarol was in one experiment 0.1 g. and in another 0.15 g. The acid was purified by crystallization from butyl alcohol followed by a recrystallization from water. The latter process was accomplished by acidifying a hot slightly alkaline solution of the potassium salt with sulfuric acid.

The risic acid melted at 256°, and when it was mixed with an authentic sample of the acid no depression of the melting point occurred. It also possessed the optical properties characteristic of risic acid. These data, determined by George L. Keenan of the Food

[4] LaForge, THIS JOURNAL, **53**, 3896 (1931).

and Drug Administration of the U. S. Department of Agriculture, are as follows. The acid crystallized from water consists of colorless square plates and rods with square ends. Most of the rods have straight extinction, although occasionally some are found that possess inclined extinction. The elongation is negative, and the indices of refraction are as follows: $\eta_\alpha$, 1.450 ($\pm$0.002) lengthwise; $\eta_\beta$, indeterminate and $\eta_\gamma$, 1.695 ($\pm$0.005) crosswise.

**Treatment of Dehydrotoxicarol with Boiling Alcoholic Potassium Hydroxide. Risic Acid.**—A suspension of 2 g. of dehydrotoxicarol in 75 cc. of a potassium hydroxide solution, made by dissolving 15 cc. of an aqueous solution of 7.5 g. of potassium hydroxide in 60 cc. of absolute alcohol, was boiled gently for thirty minutes. The dehydrotoxicarol soon dissolved, forming a dark colored solution which, after the specified time, was poured upon 100 g. of crushed ice in a separatory funnel. The mixture was diluted with water to a volume of 500 cc., acidified with sulfuric acid, and extracted with ether. The extract was washed with water and dried, after which the solvent was removed. The residue was dissolved in 20 cc. of 1% potassium hydroxide and oxidized with a solution of 4 g. of potassium permanganate in 50 cc. of hot water. After the manganese dioxide was removed, the filtrate was concentrated to 15 cc. and acidified with sulfuric acid, causing the organic acid to separate at once. In several experiments in which 2 g. of starting material was used, the yield was small and variable. Usually it was of the order of 0.1 to 0.2 g. of risic acid. After the crude material was purified by the method outlined before, it possessed the same properties as recorded for risic acid above.

**Derric Acid.**—Two and five-tenths grams of dehydrotoxicarol was treated with alcoholic potassium hydroxide, and the acidic product was separated from the reaction mixture as outlined in the preceding paragraph.

The residue from the ethereal extract was dissolved in 25 cc. of 10% potassium hydroxide solution and treated with 10 cc. of 30% hydrogen peroxide. The solution was boiled gently until frothing ceased, then it was cooled, acidified with sulfuric acid and extracted with ether. After drying, the ethereal solution was concentrated to approximately 10 cc. and allowed to crystallize. Three-tenths gram of derric acid separated, which, after recrystallization from *n*-butyl ether, melted at 167–168°. When it was mixed with pure derric acid, no depression of the melting point occurred and the substance possessed the optical properties characteristic of derric acid.[5]

## Summary

1. Dehydrotoxicarol has yielded derric, risic and 2-hydroxy-4,5-dimethoxybenzoic acids.

2. This fact demonstrates that toxicarol contains the same atomic grouping, represented by formula A in the text, as does rotenone, deguelin and tephrosin.

WASHINGTON, D. C.

[5] Clark, THIS JOURNAL, **53**, 2369 (1931).

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

# STUDIES ON THE POLYMETHYLBENZENES. V. THE SEPARATION OF MESITYLENE FROM PSEUDOCUMENE[1]

BY LEE IRVIN SMITH AND OLIVER W. CASS

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The preceding papers of this series[2] have dealt with the preparation, purification and some physical properties of most of the polymethylbenzenes containing three or more methyl groups. The work described in this paper had for its object the investigation of some derivatives of mesitylene and pseudocumene, with a view to finding a method for the preparation of these two hydrocarbons in a pure state, using as a source the mixture of the two which can be so readily obtained by the methylation of xylene.

In addition to several methods of isolating derivatives of these trimethylbenzenes from various sources, there are in the literature reports of two methods for separating the trimethylbenzenes from each other as derivatives, followed by regeneration of the pure parent hydrocarbons. The method of Jacobsen[3] involving fraction crystallization of the sulfonamides, followed by hydrolysis, was discarded because it was too long and involved. Similarly, this method as modified by Schultz[4] was found to be not only too laborious but to involve a great loss of material. Finally, the method of Armstrong and Miller[5] involving the partial sulfonation of the mixture followed by a fractional hydrolysis of the sulfonic acids, was found to be unsuitable, at least when applied to the trimethylbenzene fraction from these methylation reactions, for no pure hydrocarbons resulted when the method was used.

Nevertheless, the sulfonic acids appeared to be the most promising derivatives with which to work, for these hydrocarbons are easily sulfonated, and the sulfonic acids are well defined solids, easy to handle. Therefore it was decided to prepare the pure sulfonic acids of pseudocumene and mesitylene, and to study their physical properties, particularly the solubilities of the sulfonic acids in various solvents, in the hope of finding a suitable solvent for separating the mixture of sulfonic acids by fractional crystallization, and then to extend the studies to the fractional hydrolysis of the sulfonic acids in the hope of discovering the precise conditions of

[1] Abstracted from a thesis by Oliver W. Cass, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1931.

[2] (I) Smith and Lux, THIS JOURNAL, **51**, 2994 (1929); (II) Smith with MacDougall, *ibid.*, **51**, 3001 (1929); (III) MacDougall with Smith, *ibid.*, **52**, 1998 (1930); (IV) Smith and Lund, *ibid.*, **52**, 4144 (1930).

[3] Jacobsen, *Ann.*, **184**, 179 (1876); *Ber.*, **9**, 256 (1876).

[4] Schultz, *ibid.*, **42**, 3603 (1909).

[5] Armstrong and Miller, *J. Chem. Soc.*, **45**, 148 (1884); *Ber.*, **11**, 1697 (1878).

hydrolysis which would lead to a clean-cut separation of the two hydrocarbons in good yields. Only the two hydrocarbons mesitylene and pseudocumene needed to be considered as components of the mixture obtained by the direct methylation of xylene, for a very careful search for hemimellithene (1,2,3) in this product failed to indicate that any was present. This is another instance of the one rule which has been repeatedly found to hold in all the methylation experiments in this series, *viz.*, in the methylation of aromatic hydrocarbons with methyl chloride and aluminum chloride, ortho compounds are probably not formed at all, or if formed, occur in very small amounts.

Mesitylene sulfonic acid was found to be very readily dissolved by hot chloroform, while pseudocumene sulfonic acid is nearly insoluble in this solvent. Since the chief component of the mixture of trimethylbenzenes is pseudocumene, a separation of this sulfonic acid in a very pure form can be effected readily by washing the mixture of acids two or three times with hot chloroform. The washings contain all of the mesitylene sulfonic acid, and some pseudocumene sulfonic acid. These can be partially separated by recrystallization from chloroform, or by recrystallization from hydrochloric acid after evaporation of the chloroform, but the mesitylene sulfonic acid obtained in this way is not pure. In addition, if large amounts of material are to be separated, the volume of chloroform required is quite large. Fractional precipitation of the sulfonic acids from concentrated sulfuric acid also failed to give a good separation, for although mesitylene sulfonic acid is much the less soluble of the two, the precipitation has to be repeated several times in order to obtain the pure sulfonic acids. This involved so great a loss of material, and the use of such large quantities of sulfuric acid, that the method was abandoned.

Turning to the conditions for the hydrolysis of the two acids, the statement of Crafts[6] was verified, namely, that mesitylene sulfonic acid is easily and completely hydrolyzed by fuming hydrochloric acid at 80°, but it was found that the fuming acid could be replaced by the constant boiling hydrochloric acid without changing the temperature of hydrolysis. This was a great advantage, for it meant that the mesitylene could be steam distilled out of the reaction mixture without reducing the acid concentration below the limit needed for rapid hydrolysis. Pseudocumene sulfonic acid showed no sign of hydrolysis under these conditions, and could be recovered by chilling the acid solution left after steam distillation of the mesitylene. The use of hydrochloric acid is superior to that of sulfuric acid, for at 60° with 20% sulfuric acid, mesitylene sulfonic acid showed signs of charring, and at 80° there was considerable charring and the hydrolysis was not as rapid as with hydrochloric acid. Pseudocumene sulfonic acid, alone, was found to be perfectly stable when heated with 50% sulfuric acid

[6] Crafts, THIS JOURNAL, **23**, 248 (1901).

until a temperature of 120–125° was reached, when hydrolysis began, and at 135–145° hydrolysis became rapid and complete, with no sign of charring or tar formation. When the two sulfonic acids were mixed, however, the action of sulfuric acid was much less definite, which probably accounts for the failures to obtain either pure mesitylene or pure pseudocumene by the method of Armstrong and Miller.

The final procedure developed for the separation of these two hydrocarbons is one which takes advantage of the differences in the action of hydrochloric acid and sulfuric acid on the sulfonic acids, and the differences in temperatures at which hydrolysis to the hydrocarbons takes place. It consists in the complete sulfonation of the mixture of trimethylbenzenes, precipitation of the mixed sulfonic acids by careful dilution, filtration of these acids, followed by hydrolysis, first with constant boiling hydrochloric acid at 80°. The mesitylene sulfonic acid hydrolyzes completely under these conditions, and the mesitylene is then removed by steam distillation at 80° under reduced pressure. The residue in the distillation flask, when chilled, deposits pseudocumene sulfonic acid almost quantitatively. This is filtered off, and then hydrolyzed by steam distillation from 50% sulfuric acid at 135–145°.

This method always gave a pure pseudocumene, but frequently the mesitylene was contaminated with a small amount of material of unknown constitution, of lower boiling point (*ca.* 150–155°), much lower refractive index, and a very pungent odor. It was necessary therefore to re-sulfonate the crude mesitylene, reprecipitate the sulfonic acid, wash it with cold chloroform or cold concentrated hydrochloric acid, which removes all impurities, and then hydrolyze it to the hydrocarbon again. In this way a mesitylene which had exactly the same boiling point and refractive index was obtained from every experiment, a duplication of physical constants which cannot be obtained by synthesizing mesitylene in the usual way from acetone.

When carried out with the double sulfonation of the mesitylene, followed by refractionation of the "crude" separated hydrocarbons, the yield was about 12% pure mesitylene, 38% pure pseudocumene, with 30–35% of the mixture returned to the next run, a total recovery of 80–85%.

## Experimental Part

**The Trimethylbenzene Fraction.**[7]—This must be carefully fractionated to insure the absence of xylenes or tetramethylbenzenes, as the success of the method of separation

[7] In preparing these mixtures of trimethylbenzenes, the usual procedure was to methylate using methyl chloride, but if a supply of methyl chloride is not available it is possible to obtain consistent yields of about 15% trimethyl fraction by agitating commercial xylene (4 parts) and aluminum chloride (1 part) together at 130–140° for eight to ten hours. The mixture must be refluxed in an oil-bath, not over a free flame, and there must be vigorous stirring to avoid caking of the aluminum chloride on the bottom of the flask.

depends upon having present only mesitylene and pseudocumene. The crude trimethylbenzene fraction (b. p. 150–180°) was twice fractionated through a four-foot packed and jacketed column, only the fraction boiling at 66–68° under 22–23 mm. pressure being used for the separation.

## Preliminary Experiments

**Mesitylene Sulfonic Acid, $C_6H_2(CH_3)_3SO_3H\cdot 2H_2O$.**—Mesitylene (100 cc.) (b. p. 66.0–66.2° at 22 mm., $n_D^{20}$ 1.4965, prepared from acetone) was vigorously shaken with concentrated sulfuric acid (200 cc.) in a 500-cc. flask fitted with a short air condenser. The temperature rose rapidly to 60°, and the oil went into solution completely in five to ten minutes. A clear yellowish liquid resulted. While still warm, the contents of the flask were poured into 400 cc. of concentrated hydrochloric acid, kept at 10° or lower, or into 300 g. of ice, with constant and vigorous stirring. The sulfonic acid precipitated, and was filtered with suction through a cloth filter, pressing as dry as possible. The air-dried crude acid usually had a light pink or violet color; yield, 151 g. (90%), m. p. 76–78°. When purified by recrystallization from chloroform (50 g. acid, 200 g. chloroform), the acid (46 g.) melted sharply at 78° and was snow white. The sulfonic acid is soluble in warm concentrated or 50% sulfuric acid, warm hydrochloric acid (concentrated or 20%) and hot chloroform, and is almost insoluble in all these solvents in the cold. On heating the hydrated acid at even as low a temperature as 60° for one hour, it began to decompose, hydrolyzing to mesitylene and sulfuric acid, with some charring. The hydrate loses water over concentrated sulfuric acid at room temperature, and the dehydrated acid quickly absorbs water from the air. No definite melting point could be obtained for the anhydrous acid; the highest value obtained was 98.5–100°.

**Pseudocumene Sulfonic Acid-5, $C_6H_2(CH_3)_3SO_3H\cdot 1.5H_2O$.**—This was prepared from pseudocumene following the same directions as for the sulfonation of mesitylene, except that the sulfonation mixture was cooled before pouring onto ice or concentrated hydrochloric acid; yield, 135 g. from 100 cc. of pseudocumene (about 85%); m. p. 110–111°. Recrystallized from hot 20% hydrochloric acid, the acid crystallized as tiny white glistening plates, m. p. 111–112°. The acid contains 1.5 molecules of water of crystallization, which is slowly lost over sulfuric acid, phosphorus pentoxide, or on heating to 105° for an hour. The hydrate is stable at 80° for at least three hours, and loses only 1% in weight when heated to 90° for two hours. The melting point of the dehydrated acid is not sharp, usually 128–131°. The hydrate is soluble in cold or hot concentrated sulfuric acid, warm hydrochloric acid (concentrated or 20%), and warm 50% sulfuric acid. It is only slightly soluble in hot or cold chloroform, cold 50% sulfuric acid, and cold hydrochloric acid. Of the three isomeric pseudocumene sulfonic acids, only the one, pseudocumene sulfonic acid-5, is obtained by direct sulfonation according to these directions.

**Sulfonation of the Mixed Hydrocarbons.**—The following table shows the results of sulfonating three different fractions of the mixed trimethylbenzenes, according to the directions for sulfonating the pure hydrocarbons.

TABLE I

SULFONATION OF THE MIXED TRIMETHYLBENZENES

| Fraction | Boiling point (23 mm.), °C. | Amount used, cc. | Yield of sulfonic acid, g. | M. p., °C. |
|---|---|---|---|---|
| I | 65.0–67.5 | 50 | 60 | 95–101.5 |
| II | 67.5–68.5 | 50 | 71 | 99–103 |
| III | 68.5–75.0 | 25 | 37 | 87–93 |

**Separation of the Sulfonic Acids Using Chloroform Extraction.**—Ten grams of the acid from I was twice washed with 50 cc. of hot chloroform. There remained 6.3 g. of

white sulfonic acid, m. p. 108–110°, mixed m. p. with pure pseudocumene sulfonic acid, 110–111°.

Ten grams of the acid from II similarly yielded 7.0 g. of white sulfonic acid, m. p. 109–111°, mixed m. p. with pure pseudocumene sulfonic acid, 110–111°.

Ten grams of the acid from III, similarly yielded 6.0 g. of white sulfonic acid, m. p. 105–109°, mixed m. p. with pure pseudocumene sulfonic acid, 108–111°.

When combined (19.3 g.) and recrystallized from hot 20% hydrochloric acid, these acids yielded 15.6 g. of pure sulfonic acid, m. p. 111–112°. The chloroform washings, evaporated to 40 cc. and cooled, deposited 8.0 g. of pink sulfonic acid, m. p. 73–76°, but repeated recrystallization brought the m. p. only up to 74–77° (78° for pure mesitylene sulfonic acid) and there was much loss in the crystallization.

These experiments show that pure pseudocumene sulfonic acid can be obtained in about 50% yield from the mixture of sulfonic acids by this method, but pure mesitylene sulfonic acid cannot be so obtained.

**Hydrolysis of the Sulfonic Acids, Using Sulfuric Acid.**—One hundred cc. of the trimethylbenzene fraction was sulfonated in the usual way with 200 cc. of concentrated sulfuric acid. The mixture was then diluted with 300 cc. of water and kept at 80° for thirty minutes, after which it was rapidly steam distilled at 100–120° for fifteen minutes. The distillate contained 8 cc. of an oil, boiling at 165.1–166.1° (corr.) at 760 mm. Pure mesitylene in the same apparatus boiled at 164.1–164.5°. When the temperature of hydrolysis was raised to 140°, 78 cc. more of oil resulted in the distillate. This showed a boiling point of 67.0–71.2° at 23 mm. Pure pseudocumene boiled constantly at 68.5 (23 mm.) in the same apparatus. Thus neither the mesitylene nor the pseudocumene obtained by this method was pure.

**Hydrolysis of the Sulfonic Acids, Using Hydrochloric Acid.**—These experiments showed that mesitylene sulfonic acid was completely hydrolyzed when heated to 80° for one hour with either concentrated or 20% hydrochloric acid, and that pseudocumene sulfonic acid was unaffected under these conditions, and as these experiments led directly to the method of separation finally adopted, the details will be given in the next section dealing with the separation.

**The Separation of Pseudocumene and Mesitylene.**—Fifteen hundred grams (1728 cc.) of the trimethylbenzene mixture (b. p. 66–68° at 22 mm.) was sulfonated by shaking it with an equal volume of concentrated sulfuric acid. The temperature rose to 83° and after ten minutes nearly all the oil had gone into solution. The material, while still quite warm, was transferred to a warm separatory funnel and the unsulfonated oil (61 g., 4%) drawn off.[8]

The sulfonation mixture, after removal of this oil, was cooled to room temperature and then poured very carefully onto 1500 g. of crushed ice contained in large beakers surrounded by a freezing mixture. The dilution must be carefully done, with vigorous stirring and keeping the temperature as low as possible. The whole mixture solidified to a mass of light pink crystals which was broken up by stirring. After the temperature of the mass had fallen to 10°, the precipitate was filtered through a cloth filter on a large Buchner funnel, pressed down and sucked as free from liquid as possible. The precipitate was divided into two parts, and each part treated with a liter of 20% hydrochloric acid in a 3-necked five-liter flask, so arranged that steam could be passed through under reduced pressure. The reaction mixture was heated to 80° for thirty minutes, during which time a layer of oil appeared and the remaining sulfonic acids went into solution, giving a light pink to purple solution. Steam at 80–90° (never above 95°) was then

[8] This unsulfonated oil has a peculiar, unpleasant odor, and is probably not a polymethylbenzene, but it is important to remove it as completely as possible at this point, for otherwise it accompanies the mesitylene.

passed into the mixture for ninety minutes. The oil in the distillate was then separated, washed with water, bicarbonate and dried. It weighed 349 g. (23.3%) (from both halves of the precipitate). This was "crude" mesitylene.

The residues from this steam distillation were combined and cooled to 0°, and the solid resulting filtered off through cloth; weight, 1336 g.; m. p. 111° sharply. This solid (pseudocumene sulfonic acid) was then hydrolyzed by steam distillation from 50% sulfuric acid at 140°. The oil in the distillate, when washed and dried, weighed 639 g. (42.6%). This was "crude" pseudocumene.

The various filtrates from the sulfonic acids were combined, enough sulfuric acid added to bring the boiling point to 140°, and steam distilled at this temperature. There resulted 175 g. (11.7%) of oil, consisting of a mixture of the hydrocarbons, which was returned to the next run. The total recovery was therefore 81.6%.

The crude pseudocumene (639 g.) was carefully distilled through an efficient column. About 90% of it (568 g., 37.9%) showed a constant boiling point of 68° at 22 mm.; 168.0–168.2° at 742 mm.; $n_D^{20}$ 1.5048. This is pure pseudocumene.

The "crude" mesitylene (349 g.) is not pure, for it contains some of the pungent oil, most of which was not sulfonated in the first sulfonation. To remove this, the crude product is resulfonated, and then the sulfonic acid precipitated by pouring the reaction mixture into 800 cc. of concentrated hydrochloric acid at 0° The sulfonic acid so purified melted at 77–78°, and on hydrolysis gave 174 g. of mesitylene. Of this 163 g. (10.9%) boiled at 66.0° under 22 mm.; $n_D^{20}$ 1.4974. The filtrate from the sulfonic acid, when hydrolyzed, gave 141 g. of oil which was returned to the next run.

A summary of this and several other runs is given in Table II.

TABLE II

SUMMARY OF YIELDS IN THE SEPARATION OF MESITYLENE AND PSEUDOCUMENE

| Trimethyl fraction, g. | Yield of crude 1,3,5, % | Yield of crude 1,2,4, % | Pure 1,3,5, % | Pure 1,2,4, % |
|---|---|---|---|---|
| 377 | 8.4 | 50.4 | 5.8 | 41.9 |
| 407 | 28.0 | 40.0 | 17.9 | 37.5 |
| 200 | 17.9 | 37.6 | .. | .. |
| 400 | 21.6 | 40.4 | 12.0 | 35.1 |
| 1500 | 23.3 | 42.6 | 10.9 | 37.9 |

The purity of the two hydrocarbons was followed by means of the boiling point and the refractive index, which was found by experiment to be a linear function of the composition.

TABLE III

REFRACTIVE INDICES OF MESITYLENE–PSEUDOCUMENE MIXTURES

| Mesitylene, % | Pseudocumene, % | $n_D^{26.5}$ (obs.) | $n_D^{26.5}$ (calculated for linear function) |
|---|---|---|---|
| 100 | 0 | 1.4942 | ..... |
| 75 | 25 | 1.4961 | 1.49606 |
| 50 | 50 | 1.4980 | 1.49793 |
| 25 | 75 | 1.4999 | 1.49981 |
| 0 | 100 | 1.5017 | ..... |

## Summary

1. In the methylation of xylene using methyl chloride and aluminum chloride, no hemimellithene (1,2,3-trimethylbenzene) is formed.

2. Trimethylbenzenes can be made by simply refluxing together xylene and aluminum chloride.

3. The pure sulfonic acids of mesitylene and pseudocumene have been prepared and their properties studied.

4. The refractive index of mixtures of mesitylene and pseudocumene is a linear function of the composition.

5. Pure pseudocumene sulfonic acid may be obtained by washing the mixture of mesitylene and pseudocumene sulfonic acids with hot chloroform but pure mesitylene sulfonic acid cannot be obtained in this way.

6. A method for separating mesitylene from pseudocumene has been devised which gives both hydrocarbons in good yields and in a high state of purity, and which can be applied to the mixture of trimethylbenzenes resulting from the methylation of xylene.

MINNEAPOLIS, MINNESOTA

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

# STUDIES ON THE POLYMETHYLBENZENES. VI. THE SEPARATION OF DURENE FROM ISODURENE[1]

BY LEE IRVIN SMITH AND OLIVER W. CASS

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The fifth paper[2] of this series contained reports on methods for the separation of mesitylene and pseudocumene, the two hydrocarbons occurring in the trimethylbenzene fraction resulting from the methylation of xylene. The present paper reports a method for separating durene (1,2,4,5) and isodurene (1,2,3,5), the two hydrocarbons present in the tetramethylbenzene fraction of the methylation mixture.

The tetramethylbenzene fraction, b. p. 79–91° at 15 mm., represents from 25 to 35% of the product of the methylation of xylene. When this material is cooled to −15° or lower, durene crystallizes out and can be filtered off: about a third of the tetramethyl fraction can be recovered as crude durene, m. p. 75–77°, in this way. The filtrate from the durene is isodurene saturated with durene at the temperature of filtration—no prehnitene (1,2,3,4) is present in it. A very careful search for prehnitene was made both in the filtrate from the cold filtration, and in the "after drip"—the filtrate obtained on allowing the crude durene, while under suction, to warm slowly to room temperature in the Buchner funnel. The filtrate and after drip were first examined by fractionally distilling them and studying the detailed boiling point curves and refractive indices of the various cuts. Next, the filtrate and after drip were sulfonated, and the sulfonic acids isolated and examined for prehnitene sulfonic acid. Finally,

[1] Abstracted from a thesis by Oliver W. Cass, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1931.

[2] Smith and Cass, THIS JOURNAL, **54**, 1603 (1932)

the material in the aqueous acid filtrates from the crystallization of the sulfonic acids was hydrolyzed, and the resulting oils examined by means of boiling point curves, and refractive indices. In no case was any prehnitene found, although check experiments on samples of known composition showed that as little as 1% of prehnitene could be detected in a mixture of the tetramethylbenzenes by sulfonating the mixture, precipitating the sulfonic acids by dilution, filtering and hydrolyzing the sulfonic acids *remaining in the filtrate*. The oil resulting from this hydrolysis contains all the prehnitene and, by subjecting this to a careful fractionation, the presence or absence of prehnitene is revealed by the boiling point curve and the refractive indices of the different fractions.

Since the filtrate and "after drip" resulting from the removal of the durene contained no prehnitene, only the separation of the two hydrocarbons durene and isodurene needed to be considered. The filtrate and the after drip were combined and carefully fractionated through an efficient column. The boiling range was 79–87° at 15 mm., and the portion boiling from 82–84° (90% of the total) was used for the separation. This material had a freezing point of −25.0°, corresponding to about 90% isodurene and 10% durene; $n_D^{20}$ 1.5120.[3]

As the first step in the experiments on the separation of the hydrocarbons, each of the pure hydrocarbons was converted to the sulfonic acid and the properties of these sulfonic acids were studied. No pronounced differences in solubilities were found: all three sulfonic acids were insoluble or only slightly soluble in the following cold solvents: 50% $H_2SO_4$, 20% HCl, concentrated HCl, benzene and petroleum ether. When heated, the three acids were soluble in all these solvents except petroleum ether, but isodurene sulfonic acid began to hydrolyze when heated with the first three solvents. In cold chloroform, only prehnitene sulfonic acid is soluble, and then only slightly, while in hot chloroform, prehnitene and isodurene sulfonic acids are very soluble, and durene sulfonic acid only slightly soluble. In no case was the difference in solubility sufficient to lead to an efficient separation of the sulfonic acids. The barium salts of durene and prehnitene sulfonic acids were difficultly soluble in cold water, while that of isodurene sulfonic acid was very soluble. This difference could be made the basis of a convenient method for the separation of durene and isodurene on a small scale, but on a larger scale the difficulty of preparing and handling large amounts of these barium salts, especially when contaminated with much barium sulfate, would render the method very inconvenient.

Fractional sulfonation of durene–isodurene mixtures also failed to separate the two substances, for although the pure hydrocarbons showed a pronounced difference in the ease with which they were sulfonated, when the sulfonation was carried out on a mixture of the two, both sulfonated.

[3] Smith with MacDougall, THIS JOURNAL, **51**, 3001 (1929).

Thus 5 g. of isodurene was sulfonated completely in thirty seconds by 10 cc. of concentrated sulfuric acid, while 5 g. of durene was only about 5% sulfonated after shaking for twenty minutes with 10 cc. of concentrated sulfuric acid. But when a mixture of 5 g. of isodurene and 2.5 g. of durene was shaken for three minutes with 12.5 cc. of concentrated sulfuric acid, all of the isodurene and over half the durene was sulfonated.

Fractional hydrolysis of the mixture of sulfonic acids was also a failure as a method of separation, and for the same reasons that fractional sulfonation failed; although there is a pronounced difference in the ease with which the pure durene and isodurene sulfonic acids hydrolyze, when they are mixed, it is impossible to hydrolyze one completely without also hydrolyzing the other partially. Isodurene sulfonic acid can be hydrolyzed with 20% hydrochloric acid at temperatures as low as 60°, while durene sulfonic acid is unaffected by even concentrated hydrochloric acid at these temperatures. But when mixed and steam distilled with 20% hydrochloric acid, both sulfonic acids hydrolyze, and in an hour about two-thirds of the isodurene and half of the durene have distilled over.

Nevertheless, although neither fractional sulfonation nor fractional hydrolysis of the sulfonic acids was alone sufficient to separate durene and isodurene, it was found that by a careful combination of the two, a fairly efficient separation could be brought about. This method gives the best results when applied to the re-fractionated filtrate resulting when durene is frozen out of the original tetramethylbenzene fraction. This filtrate, b. p. 82–84° at 15 mm., $n_D^{20}$ 1.5120, consists of about 90% isodurene. The method will give 60–65% yield of "crude" isodurene (96–97% pure) and about 5% yield of durene; or, if the "crude" isodurene is re-sulfonated and the sulfonic acid again hydrolyzed, the yield is about 45% of pure isodurene practically equal in quality to the synthetic product.

## Experimental Part

**The Pure Hydrocarbons: Durene.**—This was obtained directly by freezing out the tetramethylbenzene fraction from the methylation of xylene. It was recrystallized from alcohol until the m. p. was 78–79°.

**Isodurene.**—This was synthesized from mesitylene by the method of Smith and MacDougall.[4] The bromomesitylene used as an intermediate was very carefully purified. It had a b. p. of 105.0° at 16 mm., freezing point of 0.01°; $n_D^{20}$ 1.5510 ($dn/dt$ = −0.00041 per degree rise in temperature between 15 and 30°). The purified isodurene had a freezing point of −24.1°; $n_D^{20}$ 1.5134 ($dn/dt$ = −0.00043 per degree rise in temperature between 15 and 30°).

**Prehnitene.**—This was prepared from pentamethylbenzene by the method of Smith and Lux.[5] The sample used had a freezing point of −7.0 to −7.1°; boiling point 96.5° at 25 mm., $n_D^{20}$ 1.5202 ($dn/dt$ = −0.00040 per degree rise in temperature between 15 and 30°).

[4] Smith and MacDougall, THIS JOURNAL, **51**, 3001 (1929).

[5] Smith and Lux, *ibid.*, **51**, 2994 (1925).

**Durene Sulfonic Acid,** $C_6H(CH_3)_4SO_3H \cdot 2H_2O$.—Durene (10 g.) was placed in a small beaker and covered with 50 g. (27 cc.) of a mixture of 1 part of 60% fuming sulfuric acid and 2 parts of concd. sulfuric acid. The reaction mixture was stirred vigorously, and the lumps of durene were broken up with a glass rod. The temperature rose about 20° during the sulfonation. After five minutes, the reaction mixture was poured onto 250 g. of ice and vigorously stirred. The liquid was filtered at once from the unmelted ice and the traces of unsulfonated durene. To the cold filtrate concd. sulfuric acid was slowly added, until the material set to a mass of pearly white crystals. During the addition of the sulfuric acid the temperature was kept always below 20°, and after the addition of the acid the reaction mixture was cooled to 0° and filtered with suction through cloth, pressed as dry as possible, and dried on a porous plate; yield 18.6 g. (94%), m. p. 110–112°. For purification, the acid was dissolved in the least possible quantity of 20% hydrochloric acid at 80°, the solution then cooled to 0°, filtered through cloth and dried in the air; yield of pure acid, 14 g. (70%), m. p. 113°.

**Isodurene Sulfonic Acid,** $C_6H(CH_3)_4SO_3H \cdot 2H_2O$.—Isodurene (10 g.) was sulfonated by shaking it with 20 cc. of concd. sulfuric acid in a small flask for ten minutes. The reaction mixture was poured into 20 g. of ice, the crystals filtered with suction through cloth, and dried on a porous plate; yield 18 g. (91%), m. p. 76–77°. It was purified by dissolving it in 50 cc. of cold water and passing gaseous hydrogen chloride into the ice cold solution. The white crystals were filtered, pressed out and dried in the air; yield of pure acid, 12–14 g. (60–70%), m. p. 79°.

**Prehnitene Sulfonic Acid,** $C_6H(CH_3)_4SO_3H \cdot 2H_2O$.—Prehnitene (10 g.) was sulfonated according to the directions given for isodurene; yield 18 g. (91%), m. p. 99–100°. The acid was purified according to the directions given for durene sulfonic acid; yield of pure acid, 14 g. (70%), m. p. 104°.

In all these sulfonations no traces of sulfones or other water-insoluble material were found among the reaction products. The solubilities of these sulfonic acids in various solvents, and the conditions under which they hydrolyze, have already been given.

**The Separation of Durene and Isodurene.**—The mixture of durene and isodurene used for the separation was obtained by fractionating the original methylation mixture twice, collecting the fraction boiling from 79 to 91° at 15 mm. pressure; the durene was then frozen out of this by cooling to −16° and filtering. The filtrate was then refractionated, and the portion boiling from 82–84° at 15 mm. (90% of the material) was used for this separation. The fuming sulfuric acid used in the separation consisted of a mixture of one part of "60% fuming sulfuric acid" and two parts of concd. sulfuric acid. This is the acid meant whenever the term "fuming sulfuric acid" is used.

In a two-liter flask, fitted with a short air condenser, was placed 500 g. of the durene–isodurene mixture. To this was added 500 cc. of the fuming sulfuric acid, and the flask then shaken vigorously for three minutes. The temperature rose to 80°, and nearly all of the oil went into solution. Without cooling, the contents of the flask was poured out, with vigorous stirring, upon 1500 g. of finely chipped ice in a 4-liter beaker. Stirring and cooling were continued until the temperature fell to 5°, and the material was then rapidly filtered with suction through a cloth filter. This separated the unsulfonated material, ($R_1$), chiefly durene, from the sulfonated material in the filtrate ($F_1$).

The filtrate ($F_1$) was at once treated with 250 cc. of concd. sulfuric acid, which was added with vigorous stirring, keeping the temperature below 25°. The whole mixture set to a mass of crystals, which was broken up, cooled to 5°, and filtered with suction through cloth, pressing as dry as possible, (precipitate $R_2$, filtrate $F_2$).

The precipitate $R_2$ was transferred at once to a two-liter flask arranged for steam distillation, 500 cc. of 20% hydrochloric acid was added, and the mixture steam distilled for one hour. The residue in the flask ($R_3$) was set aside. The oil in the distillate ($D_1$)

was separated, washed with bicarbonate and dried over calcium chloride. This oil weighed 319 g. (63.8% of the wt. of starting material); freezing point −26.0, which corresponds to about 96% isodurene.

This oil $D_1$ was then re-sulfonated exactly as described for the mixture with which the separation started, using everywhere proportionate amounts of reagents. The sulfonic acid obtained from the re-sulfonation melted sharply at 78.5° (recrystallized isodurene sulfonic acid melts at 79°), and on hydrolysis gave 240 g. (48% of the wt. of the starting material) of dry oil, which was carefully fractionated. At 22–23 mm. 95% of this oil boiled between 90–91°. The middle fraction was collected (223 g., 44.6%) and this showed a freezing point of −24.08° (the freezing point of synthetic isodurene is −24.0±0.1°).[4] The low-boiling material from this fractionation, and the residue in the distilling flask, 14 g. in all, were put back in stock for the next run.

The unsulfonated oils, $R_1$ from the original sulfonation, and a corresponding oil from the re-sulfonation, were combined, washed with bicarbonate and dried; wt., 67.6 g. (13.5% of the starting material). On cooling to −10° and filtering, 28 g. of crude durene (m. p. 70–73) was obtained. The filtrate from this was returned to stock for the next run.

The acid filtrates from the precipitation of the sulfonic acids, as well as the residues from the steam distillations, were all combined, enough sulfuric acid added to bring the b. p. to 140°, and steam passed through at 140° until no more oil was distilled over. The oil in the distillate was separated, washed with bicarbonate, and dried. It weighed 60.2 g. (12% of the starting material), and was added to stock for the next run. Thus the yields in the separation were: 223 g. pure isodurene (44.6%); 28 g. crude durene (5.6%); and 100 g. of mixture (20%) returned to the next run. Total recovery, 351 g. (70%). The loss was thus 30% and this was due almost entirely to inefficient condensation during the long steam distillations and vacuum fractionations. If a trap cooled with carbon dioxide snow had been inserted in the exit of the distilling train, a much higher recovery could probably have been obtained, for there was no organic material left in the final residues from the steam distillations.

It is exceedingly important for a successful separation that the directions as to amounts of reagents, and *particularly the time of contact with the reagents*, be followed exactly, for both durene and isodurene sulfonic acids, in contact with sulfuric acid, undergo the Jacobsen rearrangement, giving prehnitene. The separation should never be interrupted immediately after a sulfonation or after a filtration of the sulfonic acids from the sulfuric acid solution, and the best results are obtained when the whole separation is carried straight through without any interruption. The table summarizes a few runs.

TABLE I

THE SEPARATION OF DURENE AND ISODURENE

| Run | Mixture, g. | Crude isodurene (96–97%) | Pure isodurene, g. | Pure (recryst.) durene, g. |
|---|---|---|---|---|
| 1 | 200 | 102.2 | 115.4 (m. p. −24.17°) | 11 |
| 2 | 200 | 103.4 | | |
| 3 | 500 | 319.0 | 223 (m. p. −24.08°) | 16 |

It was found, in this work, that the only property of isodurene suitable for testing its purity was the freezing point. The refractive index of mixtures of durene and isodurene is practically the same as that of pure isodurene for concentrations of durene as high as 20%, and very little information about the purity of a specimen can be obtained from the boiling point, but the freezing point of the specimen furnishes an accurate method of analysis.

## Summary

1. A method for separating durene from isodurene has been devised, which gives a pure isodurene in yields of about 45%, when applied to the refractionated filtrate obtained by freezing out the durene from the tetramethylbenzene fraction resulting from the methylation of xylene.

2. In the methylation of xylene using methyl chloride and aluminum chloride no prehnitene (1,2,3,4) is formed.

3. The pure sulfonic acids of each of the tetramethylbenzenes have been prepared, and some of their properties studied.

MINNEAPOLIS, MINNESOTA

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

# THE JACOBSEN REACTION. II[1]

BY LEE IRVIN SMITH AND OLIVER W. CASS[2]

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In the first paper of this series[3] a report was made of a preliminary study of the Jacobsen reaction when applied to pentamethylbenzene, but as the purpose of that work was to develop a method for preparing prehnitene, the study was limited to the one hydrocarbon, pentamethylbenzene. This study has now been extended to other polymethylbenzenes, and the present paper reports some of these results.

The results of Jacobsen and other workers in this field, together with references to the literature, have been given in detail in the paper by Smith and Lux. In the case of the hydrocarbons studied so far in this Laboratory, it has been found that the rearrangement of methyl groups caused by sulfuric acid (the "Jacobsen Reaction") is limited to pentamethylbenzene, durene and isodurene. The hydrocarbons mesitylene, pseudocumene, prehnitene and hexamethylbenzene do not rearrange when in contact with concd. sulfuric acid at room temperatures for over ten days. Of the three hydrocarbons which did undergo a rearrangement, pentamethylbenzene was the only one from which the chief products of the reaction were a more highly methylated benzene and a less highly methylated one. Durene and isodurene gave prehnitene sulfonic acid as the main reaction product, involving only a shift of a methyl group within the molecule.

In the case of durene and isodurene, it was found to be the sulfonic acid which rearranged, and not the hydrocarbon, as Jacobsen maintained. If the pure sulfonic acids (either the anhydrous or hydrated forms) of these

[1] Paper VII on the Polymethylbenzenes. VI, THIS JOURNAL, **54**, 1609 (1932).

[2] Abstracted from a thesis by Oliver W. Cass, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1931.

[3] Smith and Lux, THIS JOURNAL, **51**, 2994 (1929).

hydrocarbons were mixed with phosphorus pentoxide, or simply kept in a desiccator over this reagent, the reaction proceeded as usual. But if the hydrocarbons themselves were boiled with phosphorus pentoxide, or kept in a desiccator over either phosphorus pentoxide or sulfuric acid, no change occurred even after standing for months. Durene sulfonic acid was acted upon almost at once by warm concd. sulfuric acid, while durene, which is only slowly sulfonated by concd. sulfuric acid, would undergo the Jacobsen reaction only very slowly. On the other hand, fuming sulfuric acid, which sulfonates durene rapidly, also acted rapidly on either durene or its sulfonic acid with liberation of much sulfur dioxide, causing the Jacobsen reaction to take place. Warm, concd. sulfuric acid, which sulfonates isodurene rapidly, caused the Jacobsen reaction to take place with either isodurene or its sulfonic acid. Furthermore, the reagent—phosphorus pentoxide or sulfuric acid—is necessary, for both the hydrated and the dehydrated durene and isodurene sulfonic acids were perfectly stable when kept in a sealed tube for a period of eight months, while all of the hydrated sulfonic acids have been kept in glass stoppered bottles for over a year with no decomposition whatever. Nor does the water of hydration have any effect upon the reaction, for both the hydrated and dehydrated sulfonic acids behave in the same way toward phosphorus pentoxide or sulfuric acid.

In all the Jacobsen reactions, much sulfur dioxide is evolved, and the next experiments were directed toward determining the amount of this gas, and whether or not it was the only gaseous product. The reaction between durene and sulfuric acid was allowed to take place at room temperature, and the gaseous products were swept out with a stream of dry air, free from carbon dioxide. The exit gases were then passed through potassium hydroxide solution, which was analyzed from time to time. The experiment was run for twenty-five days, as at room temperature the reaction is a very slow one. The gas evolved was found to be chiefly sulfur dioxide. In spite of the oxidizing stream of air used to sweep the apparatus, the ratio of sulfate sulfur (total sulfur dioxide as barium sulfate after iodine titration) to sulfite sulfur (sulfur dioxide by direct iodine titration) was only 1.13 to 1.00, showing that sulfur trioxide could not be present in the evolved gases in very appreciable amounts. In a second quantitative experiment, durene sulfonic acid was used with phosphorus pentoxide and the apparatus swept with a current of pure, dry hydrogen. In this case the ratio of sulfate to sulfite sulfur was 1.03 to 1.00. It therefore was apparent that the sulfur is liberated as sulfur dioxide, and that this came from the reduction of the sulfonic acid group, and not from the sulfuric acid, as reported by Smith and Lux in the case of pentamethylbenzene. In none of these experiments was any hydrogen sulfide or free sulfur found.

The mole ratios between the durene sulfonic acid used and the sulfur dioxide formed when phosphorus pentoxide acted upon the sulfonic acid,

were, in two separate experiments, 1 to 0.342 and 1 to 0.356. In the twenty-five day experiment with durene and sulfuric acid, the ratio between the durene used and the sulfur dioxide produced in twenty-five days was 1 to 0.290, but this particular reaction was very slow under the conditions of the experiment and at the end of twenty-five days it was not complete. Whether the ratio of about three moles of hydrocarbon or sulfonic acid to 1 of sulfur dioxide is really a constant, and what bearing this has upon the mechanism of the reaction, cannot yet be decided. But the evolution of sulfur dioxide in large amounts does appear to be an essential part of the Jacobsen reaction (or of a simultaneous reaction, the conditions for which are the same as those for the Jacobsen reaction) because in every case in which no rearrangement of methyl groups took place, no sulfur dioxide was evolved, while in every case of actual rearrangement, large amounts of sulfur dioxide were evolved.

Since the sulfur dioxide was formed by the reduction of the sulfonic acid group, experiments were next directed toward determining what was oxidized in the process. This was done in the streaming experiments by checking the gain in weight of the potassium hydroxide bulb against the total sulfur calculated back as sulfur dioxide, and it was found that 95% of the total gain in weight was accounted for by the sulfur as sulfur dioxide, leaving only about 5% for carbon dioxide. This 5% difference in weight, which should be due to carbon dioxide, amounted to 0.0019 mole of carbon dioxide, which was only 7% of the number of moles of sulfur dioxide produced. Hence the oxidation product was not carbon dioxide, but most likely was water formed by the oxidation of hydrogen. If so this hydrogen must have been eliminated from a methyl group, or from the open positions on the benzene ring, which might well lead, in either case, to the linkage of several durene residues, producing compounds of high molecular weight. The fact that the reaction took place only under strong dehydrating conditions is not inconsistent with the hypothesis that water is one of the products of the reaction which leads to the sulfur dioxide, but there is the possibility that the amorphous by-products may be the oxidation product, as these have not yet been shown to be oxygen free.

In addition to the gaseous reaction products and the rearranged polymethylbenzenes there were formed two other products whenever the Jacobsen reaction took place. One of these products was an intensely black, water-soluble substance, formed in small amounts, which could be removed from the aqueous solutions only by repeated treatments with decolorizing carbon. The other product was a brownish red amorphous material, insoluble in water, which was formed in amounts corresponding to 10 to 30% of the weight of the starting material. Attempts to purify this material were unsuccessful: it does not melt or sublime even when heated to a red heat (*i. e.*, until the melting point tube softened and col-

lapsed) and all attempts to secure pure products of any melting point by recrystallization from various organic solvents failed. From its behavior on heating, and its qualitative analysis, it is believed to be a sulfur-free material of high molecular weight.

The only sulfonic acid that was isolated in large amounts from the Jacobsen reaction upon durene, isodurene or pentamethylbenzene was prehnitene sulfonic acid. Since both durene and isodurene give the same product as a result of the Jacobsen reaction, the mixture of the two hydrocarbons offers a much more convenient source for making prehnitene than the method using pentamethylbenzene, as previously described by Smith and Lux, for this mixture is much more easily obtained in quantity than is pentamethylbenzene.

When the action of aluminum chloride and methyl chloride in the methylation of hydrocarbons is compared with the results of this study on the Jacobsen reaction, the curious fact appears that the orientations of the methyl groups in the comparable products is opposite in the two cases: the direct methylation has been found repeatedly to give little or no *ortho* methylated benzenes (no 1,2,3-trimethylbenzene, no 1,2,3,4-tetramethylbenzene), while when the tetramethylbenzenes undergo the Jacobsen reaction, the shift is completely in the direction of the 1,2,3,4-compound.

These studies are being continued in this Laboratory, and investigations of the reaction with other classes of compounds are under way, as well as investigations designed to throw light on the mechanism of this reaction.

## Experimental

**Hydrocarbons Not Undergoing the Jacobsen Reaction.**—Into a 100-cc. flask was placed 10 g. of the sample, together with 30 cc. of concd. sulfuric acid. The flask was fitted with a calcium chloride tube, and then allowed to stand for ten days with occasional shaking.

(a) Pseudocumene, b. p. 68° at 22 mm. Sulfonated at once, going into solution.
(b) Mesitylene, b. p. 66° at 22 mm. Sulfonated at once, going into solution.
(c) Prehnitene, m. p. −7.1°. Sulfonated at once, going into solution.
(d) Hexamethylbenzene, m. p. 160–162°. No apparent change.

In no case did the material blacken, though in all cases a light yellowish-brown color developed. There was no odor of sulfur dioxide from any of the samples except the hexamethylbenzene, and in this case it was very slight. At the end of ten days, a, b and c had crystallized. Each sample was treated with 50 g. of ice, the sulfonic acid filtered off and dried on porous plates. From a there resulted 12.5 g. of pseudocumene sulfonic acid-5; m. p. 110–11°; from b, 13.2 g. of mesitylene sulfonic acid, m. p. 76–78°; from c, 11.8 g. of prehnitene sulfonic acid, m. p. 101–103°. Sample d was washed out into 200 cc. of water, filtered, washed with water and dried. There remained 10 g. of hexamethylbenzene, m. p. 158–160°. In none of the four cases had any rearrangement taken place.

**The Jacobsen Reaction upon Durene, Using Concd. Sulfuric Acid at Room Temperature.**—Into a small flask was placed 12.5 g. of durene (0.093 mole) and 25 cc. of concd. sulfuric acid was then added. The flask was arranged so that dry carbon dioxide-free air could be swept through it and the gaseous products of the reaction then passed

through an absorption bulb containing aqueous potassium hydroxide solution. This bulb was weighed from time to time, and the gain in weight noted. The reaction was allowed to proceed at room temperature for twenty-five days, with intermittent sweeping, during which time the absorption bulb was refilled twice. After each refilling, and at the end of the experiment, the contents of the bulb were analyzed, as follows: the alkaline solution from the bulb was made up to 500 cc. and aliquots removed for titrations. One portion was tested with lead acetate for sulfides, with negative results. Two portions were analyzed for sulfite ion by acidifying with sulfuric acid and titrating with standard iodine solution. Two other portions were then treated with an excess of iodine solution, and the total sulfate content determined by precipitation as barium sulfate in the usual way. These analyses were carried out each time the bulb was refilled, and at the end, and the results are given in the table.

TABLE I

RESULTS OF ANALYSIS OF THE GASEOUS PRODUCTS OF THE REACTION

| Time, hours | Gain in weight of the bulb, g. | $SO_2$ (titration), g. | $SO_2$ (as $BaSO_4$ after oxidation), g. |
|---|---|---|---|
| 0–198 | 0.6067 | 0.4613 | 0.5329 |
| 198–304 | .5653 | .5105 | .5600 |
| 304–515 | .6412 | .5951 | .6380 |
| Totals | 1.8132 | 1.5669 | 1.7309 |
| | Moles $SO_2$ | 0.024 | 0.027 |

Hence the chief gaseous product was sulfur dioxide, 95% of the total gain in weight being accounted for by the total sulfur dioxide found by precipitation. The 5% difference in weight, 0.0823 g. which should have been due to carbon dioxide, was equal to 0.0019 mole of carbon dioxide, or only 7% of the number of moles of sulfur dioxide found by precipitation. As 90% of the total sulfur was found as sulfite, in spite of the oxidizing action of the stream of air, it was safe to conclude that the sulfur was liberated as sulfur dioxide and not sulfur trioxide, nor as free sulfur, or hydrogen sulfide, since the tests for sulfides were all negative, and there was never any evidence of free sulfur.

The reaction mixture in the flask was added to 200 cc. of cold water. A reddish-brown, insoluble substance precipitated, which was filtered, washed with water and dried, 2.0 g. This brown powder could be heated to the softening point of glass without melting, and to 220° at 4 mm. pressure without subliming or distilling. The filtrate from this material was jet black. It was decolorized by several treatments with decolorizing carbon and then evaporated in a beaker over an open flame until the boiling point reached 115°. On cooling, the material solidified to a mass of pearly white crystals of sulfonic acid, which was filtered through cloth and dried on a porous plate: wt. 16.2 g., m. p. 97–98°; the mixed m. p. with prehnitene sulfonic acid (103–104°) was 101–103°. It was thus impure prehnitene sulfonic acid. To identify it further, it was hydrolyzed by the "flash" method of Smith and Lux,[3] yielding 6.3 g. colorless oil. This oil was then distilled from a small flask. The first few drops came over at 160–163°, and the temperature then rose rapidly to 198° at which point the main portion distilled. The first few drops were nitrated, yielding a trinitro compound, m. p. 183–184°; mixed m. p. with trinitropseudocumene (183–184°), also 183–184°. The small amount of low boiling material was therefore pseudocumene. A few drops of the main distillate were nitrated in the same way, giving a dinitro compound, m. p. 174–175°; mixed m. p. with dinitroprehnitene (174–176°), also 174–175°. The main distillate had a freezing point of −10°, against −6.4° for pure prehnitene. The refractive index, $n_D^{22}$ 1.5194, is also the value for the pure hydrocarbon. There was no doubt, therefore, that the main product of the Jacobsen reaction upon durene was prehnitene sulfonic acid, contaminated

with a small amount of pseudocumene sulfonic acid. The theoretical yield of prehnitene sulfonic acid from 0.093 mole of durene assuming only a rearrangement, is 23.25 g. [$C_6H(CH_3)_4SO_3H \cdot 2H_2O$ = 250]. Neglecting the small amount of pseudocumene sulfonic acid, the 16.2 g. prehnitene sulfonic acid obtained is a 70% yield. If the weight of durene used (12.5 g.) is corrected for the 2 g. of brown amorphous powder formed, then the theoretical yield of prehnitene sulfonic acid is 19.6 g. and the amount actually obtained is 83% of this. It therefore follows that in the Jacobsen reaction on durene by far the main reaction is merely rearrangement to prehnitene sulfonic acid; the formation of the brown powder accounts for about one-sixth of the durene used; and finally, pseudocumene sulfonic acid is formed in very minor amounts.

**The Behavior of Durene Sulfonic Acid Hydrate When Kept over Phosphorus Pentoxide at Room Temperature.**—Two 18-g. samples of durene sulfonic acid hydrate ($2H_2O$) m. p. 113°, and free from sulfates, were placed in a desiccator over phosphorus pentoxide for two months. After two weeks the material began to darken, the odor of sulfur dioxide was noticeable, and the phosphorus pentoxide began to turn pink. At the end of six weeks the sulfonic acid was jet black, with shining crystals of durene scattered through it, and the drying agent was a deep brown. At the end of eight weeks the samples were removed. Each had lost 3.0 g. in weight. They were washed with petroleum ether, which, on evaporation, left fairly pure durene (m. p. 75–77°). The black material insoluble in petroleum ether was treated with 100 cc. of water, the insoluble material filtered off, washed and dried. It was a brown powder which did not melt at 350°. The aqueous filtrate from this was decolorized, evaporated until the boiling point was 115° and cooled. The resulting white solid was filtered through cloth, and dried on a porous plate. It was prehnitene sulfonic acid, mixed m. p. with a pure specimen (103–104°), 100–103°. The results of these two experiments are given in Table II.

TABLE II

RESULTS OF THE ACTION OF PHOSPHORUS PENTOXIDE ON DURENE SULFONIC ACID HYDRATE AT ROOM TEMPERATURE

| Sulfonic acid Used, g. | Sulfonic acid Lost, g. | Durene recovered, g. | Sulfonic acid, g. | M. p., °C. | Insol. brown powder, g. |
|---|---|---|---|---|---|
| 18.0 | 3.0 | 2.8 | 6.6 | 99–101 | 2.2 |
| 18.0 | 3.0 | 3.0 | 7.0 | 99–101 | 1.8 |

Thus at room temperature, over a period of eight weeks in a dehydrating atmosphere, durene sulfonic acid gave essentially the same products as are obtained when durene is kept in contact with sulfuric acid. Results entirely comparable to these were obtained when the anhydrous sulfonic acids were allowed to stand over phosphorus pentoxide.

**The Behavior of Durene Sulfonic Acid Hydrate in Contact with Phosphorus Pentoxide.**—Into a small flask was placed 12.5 g. of durene sulfonic acid hydrate (0.05 mole), then 30 g. of phosphorus pentoxide was dropped upon it, the flask quickly closed with a stopper arranged to admit a current of gas, and the whole apparatus connected to a weighed potash bulb. The gases were swept out with a stream of pure dry hydrogen. The contents of the flask darkened rapidly and the temperature rose. Some durene sublimed on the walls of the flask. After three hours the reaction mixture was worked up as described in the preceding paragraph, and the contents of the potash bulb analyzed for sulfite by direct titration and for total sulfur by precipitation as barium sulfate after oxidation. Found, $SO_2$ as sulfite, 1.111 g.; total $SO_2$ as $BaSO_4$, 1.140 g. Mole ratio sulfite to sulfate, 1.00 to 1.03. Mole ratio between the sulfonic acid used and $SO_2$ formed, 1.00 to 0.356. The contents of the flask, when separated, gave 0.9 g. of durene, 4.0 g. of the brown powder, and 3.8 g. of prehnitene sulfonic acid, m. p. 100–101°. Again

the results were qualitatively the same as those obtained in the regular Jacobsen procedure, or when the sulfonic acid is kept in a desiccator over phosphorus pentoxide. In another similar experiment, the results were practically the same: the mole ratio of the durene sulfonic acid used to $SO_2$ evolved being 1 to 0.342.

**The Jacobsen Reaction upon Isodurene, Using Concd. Sulfuric Acid at Room Temperature.**—Twenty-five grams of isodurene was placed in a flask with 50 cc. of concd. sulfuric acid and shaken for five minutes, when the hydrocarbon went into solution. Sulfur dioxide was evolved, and the mixture slowly turned black. After two days it had solidified, and after standing for eight days longer the mass of crystals was broken up and extracted with petroleum ether. Only a minute amount of high-boiling oil was removed by the petroleum ether. The material insoluble in petroleum ether was diluted with 200 cc. of water and filtered, yielding 7.0 g. of brown, high melting insoluble material. The jet black filtrate was decolorized and then evaporated until the boiling point reached 115°. On cooling, 23 g. of a sulfonic acid resulted, m. p. 97.5–100.5°; mixed m. p. with prehnitene sulfonic acid (103–104°), 101–103°. The theoretical yield of prehnitene sulfonic acid hydrate ($2H_2O$) from 25 g. of isodurene (assuming only the rearrangement and sulfonation) is 46.6 g.; theoretical yield from 18 g. of isodurene (correcting for the 7 g. brown powder formed) 33.5 g. The amount obtained, 23 g., is 50% yield from 25 g. isodurene, and 70% yield from 18 g. of isodurene. Thus the same conclusions may be drawn from the experiments upon isodurene as from those on durene: the main reaction is merely a rearrangement to prehnitene sulfonic acid, and the same high melting brown powder is formed as the chief by-product.

**The Jacobsen Reaction on Mixtures of Durene and Isodurene.**—Since both durene and isodurene gave prehnitene through the Jacobsen reaction, these experiments were designed to utilize the tetramethylbenzene fraction from the methylation of xylene, as a source for prehnitene. After cooling this fraction to about −15° and filtering off the durene, the filtrate so obtained consists of about 90% isodurene and 10% durene. One experiment will be described, and the results of others given in a table: 100 g. of this filtrate (b. p. 82–84° at 15 mm.) was shaken for five minutes with 100 cc. of a mixture of 2 parts of concd. sulfuric acid and 1 part "60% fuming $H_2SO_4$." The hydrocarbons rapidly dissolved, after which the reaction mixture was kept at 80°. After four hours, the mixture solidified, and at the end of nine hours the black solid was broken up and poured out upon 500 g. of ice. The brown insoluble material (wt. 18 g.) was filtered off. The black filtrate was not decolorized, but was at once cooled to +10° and treated with 250 cc. of cold concd. sulfuric acid. The resulting black crystalline precipitate of sulfonic acid was filtered off through cloth and pressed as dry as possible; m. p. 98–100°. It was then dissolved in 200 cc. of warm water and hydrolyzed at 145–150° by the "flash" method of Smith and Lux.[3] The oil in the distillate, after drying, weighed 65.2 g. After the residue in the distillation flask had cooled, it deposited 7.0 g. of black solid. The 65.2 g. of oil was carefully fractionated, as follows.

TABLE III

FRACTIONATION OF CRUDE PREHNITENE

| Fraction | B. p., 25 mm., °C. | Wt., g. | $n_D^{25}$ | Freezing point, °C. |
|---|---|---|---|---|
| I | 66–75 | 8.0 | 1.5051 | |
| II | 75–94 | 4.0 | 1.5110 | |
| III | 94–96.4 | 6.8 | 1.5167 | −16 |
| IV | 96.4 | 41.4 | 1.5196 | − 7.2 |
| V | Residue | 3.0 | 1.5210 | −10.0 |

Fraction IV was very good prehnitene, showing a freezing point of −7.2° against −6.4° for the pure hydrocarbon. Fractions I and II contained a trimethylbenzene,

presumably pseudocumene. In the table below the results of some other runs are summarized; these data show that the best yields of prehnitene result when the temperature is from 70 to 90°, and the time about nine hours, although the time may be shortened considerably by operating at the higher temperatures.

TABLE IV

RESULTS OF THE CONVERSION OF DURENE–ISODURENE MIXTURES TO PREHNITENE

| Wt. of tetramethyl filtrate, g. | Time | Temp., °C. | Prehnitene obtained, g. |
|---|---|---|---|
| 100 | 3 days | 25 | Little |
| 50 | 4 hours | 80 | 13.2 |
| 100 | 2 hours | 90 | 38.6 |
| 50 | 9 hours | 70 | 16.0 |
| 50 | 9 hours | 70 | 21.2 |
| 100 | 9 hours | 80 | 41.4 |

Thus a yield of over 40% of prehnitene can be obtained in this way, and this is the most convenient method yet discovered for the preparation of this hydrocarbon.

## Summary

1. The Jacobsen reaction can be divided into at least two rearrangements: (a) the shift of methyl (alkyl) groups from molecule to molecule, giving higher and lower methylated benzenes, and (b) the shift of methyl groups within a molecule to an arrangement more stable toward sulfuric acid or other strong dehydrating conditions.

2. Of the polymethylbenzenes, only durene, isodurene and pentamethylbenzene undergo the reaction, the first two reacting according to (b), giving prehnitene, and the pentamethylbenzene reacting according to (a), giving prehnitene and hexamethylbenzene.

3. Mixtures of durene and isodurene can thus be used as a source for prehnitene.

4. The hydrocarbons are not the only products of the reaction, but are accompanied by sulfur dioxide, a black, water-soluble material, and a brown amorphous water-insoluble material, the last occurring in amounts of from 10 to 30% of the total material recovered.

5. It is the sulfonic acid which rearranges, and not the hydrocarbon.

6. The dehydrating agent—phosphorus pentoxide or sulfuric acid—is necessary, for the sulfonic acids alone are stable.

7. The shift of the methyl groups is accompanied by reduction of the sulfonic acid group of part of the material used.

8. The orientation effects of the Jacobsen reaction and those of the direct methylation of benzene hydrocarbons, are entirely opposite in the case of tetramethylbenzene.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

# STUDIES RELATING TO ORGANIC GERMANIUM DERIVATIVES. V. REACTION OF SODIUM TRIPHENYL GERMANIDE WITH HALOGENATED METHANES IN LIQUID AMMONIA

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## I. Introduction

Triphenylgermanium is an amphoteric group which forms non-salt-like compounds with the halogens and true salts with the alkali metals.[1] The latter compounds, of which sodium triphenyl germanide is an example, are valuable as reagents for introducing the triphenylgermanium group into combination with carbon and perhaps other elements. In principle, the reactions proceed as follows

$$R_{4-n}CX_n + n\mathrm{NaGe}(C_6H_5)_3 = n\mathrm{NaX} + R_{4-n}C[\mathrm{Ge}(C_6H_5)_3]_n \qquad \text{(Ia)}$$

Here R represents hydrogen or a hydrocarbon group and X represents a halogen atom. With monohalides, the above reaction ordinarily proceeds quantitatively in liquid ammonia solution.

It might be expected that the same type of reaction would occur in the case of more highly halogenated organic derivatives. Thus, sodium trimethyl stannide reacts readily with methylene chloride in accordance with equation Ia[2] although complications result when it reacts with chloroform.[3] On the other hand, sodium triphenyl stannide reacts with chloroform in accordance with equation Ia while, in the case of carbon tetrachloride, coupling between tin and carbon fails to occur.[4]

In the present investigation, a study has been made of the reactions of liquid ammonia solutions of sodium triphenyl germanide with methyl iodide, ethyl bromide, methylene chloride, chloroform and carbon tetrachloride. The reactions with methylene chloride and ethyl bromide were found to proceed normally and quantitatively. On the other hand, in the case of both methylene chloride and chloroform, side reactions occur in which the solvent is involved. With methylene chloride, the chief product is di-triphenylgermanylmethane, along with some triphenylgermanylmethane and triphenylgermanylamine. In the case of chloroform, no tertiary substitution product is obtained. The products, in fact, are the same as those obtained with methylene chloride although in somewhat different proportions. With carbon tetrachloride a mixture of reac-

[1] W. H. Kahler has shown that sodium triphenyl germanide is more highly ionized in liquid ammonia than are ordinary inorganic salts, such as the alkali metal halides (Thesis, Brown University, 1930).

[2] Kraus and Neal, THIS JOURNAL, **52**, 695 (1930).

[3] Kraus and Neal, *ibid.*, **52**, 4426 (1930).

[4] Harry Eatough, Thesis, Brown University, 1929.

tion products was obtained that were not completely separated. Triphenylgermanylamine appeared to be formed and there was evidence of the formation of small quantities of di-triphenylgermanylmethane and triphenylmethylgermane.

## II. Materials

**Tetraphenylgermanium.**—The source material for the present investigation was tetraphenylgermanium prepared by the method of Kraus and Foster.[5] After decomposing the excess reagent, the product was thoroughly washed with water and dried. The dry material was washed with low-boiling petroleum ether in order to remove diphenyl. The tetraphenylgermane was then extracted with trichloroethylene.

**Triphenylgermanium Bromide.**—This compound was prepared according to the method of Kraus and Foster.[5] Equivalent quantities of tetraphenylgermane and bromine were boiled for fifteen hours in twenty times their combined weight of carbon tetrachloride. No diphenylgermanium dibromide was formed and 80% of the tetraphenylgermane was converted to the desired bromide while the remainder was recovered as unreacted material. The triphenylgermanium bromide was freed from tetraphenylgermane by sublimation in a high vacuum at 150° (m. p. 138°).

The attempt was made to prepare triphenylgermanium bromide by the interaction of tetraphenylgermanium and germanium tetrabromide. According to Eatough,[4] the corresponding reaction proceeds readily in the case of tin. After heating to 265° for more than fifteen hours, only about 20% of the tetraphenylgermanium was converted to the bromide. Some dibromide was also formed.

**Hexaphenylgermanoethane.**—This compound was prepared according to the method of Morgan and Drew[6] by the reduction of triphenylgermanium bromide with metallic sodium in boiling xylene. Histological xylene was purified by boiling with sodium previous to distillation. The reduction must be carried out under an atmosphere of nitrogen and with rigid exclusion of oxygen. In one preparation, 86% of hexaphenylgermanoethane (m. p. 336°) was obtained and 12% of triphenylgermanium bromide was recovered unconverted.

**Sodium Triphenyl Germanide.**—Sodium triphenyl germanide was prepared by the method of Kraus and Foster[5] by treating carefully purified hexaphenylgermanoethane with sodium in liquid ammonia. The sodium is introduced in small pieces so as to avoid a high concentration since, otherwise, phenyl groups are split off from the germanium atom. Reaction proceeds somewhat slowly on account of the low solubility of the germanoethane. The salt is very reactive toward oxygen, which needs to be excluded rigidly.

**Apparatus and Procedure.**—The apparatus employed in carrying out the reaction between sodium triphenyl germanide and the various halogenated organic derivatives is sketched in the accompanying figure (Fig. 1). The sodium triphenyl germanide is prepared in the reaction tube A and the reaction with the organic halide is carried out in the same tube. In preparing the sodium triphenyl germanide, the hexaphenylgermanoethane is introduced into the reaction tube while an equivalent quantity of sodium, cut in small pieces, is introduced into the addition tube B, which is fitted to the reaction tube by means of a ground glass joint C. By turning the addition tube through a suitable angle, the sodium may be added to the reaction mixture piece by piece. Ammonia is introduced into the reaction tube through the stirring tube D and is condensed under a pressure regulated by the height of mercury in the trap E. The reaction tube is surrounded by a bath of liquid ammonia contained in the Dewar tube F.

[5] Kraus and Foster, THIS JOURNAL, **49**, 457 (1927).

[6] Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

The organic halide may be added directly from a pipet by replacing the addition tube B by the open end tube shown as 2b. Under these conditions, a stream of ammonia gas is kept issuing through the tube G. In most instances, however, with volatile organic halides, it is preferable to introduce the halide by means of a stream of ammonia vapor. The liquid is introduced into the tube H through the side arm I, which is then sealed off. By closing stopcocks J, K and L, ammonia vapor passes over the liquid in H and carries the vapors into the reaction tube A, where they are condensed.

The tube M is a buret for collecting any gases that may be formed in the course of the reaction. The bottom of this tube sets in a vessel containing freshly boiled water W. The reaction tube is attached to the system by means of de Khotinsky cement at N and O. If desired, the reaction tube may be detached and weighed. The ammonia system is provided with a safety trap P and the vacuum system is provided with a McLeod gage.

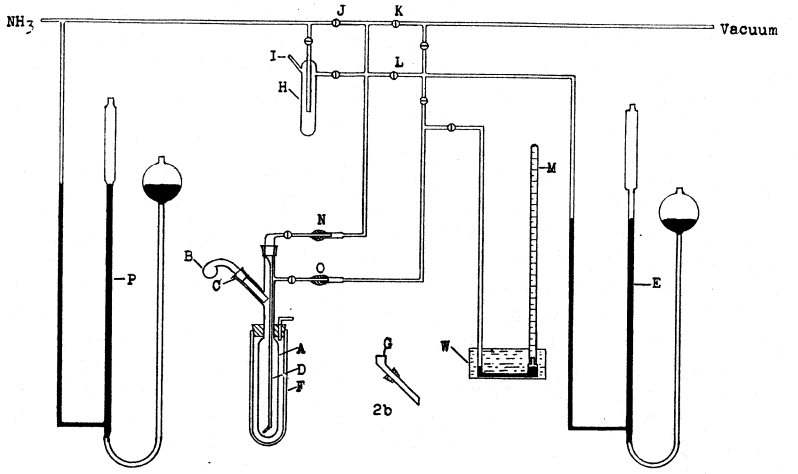


Fig. 1.—Sketch of apparatus.

When the sodium triphenyl germanide has been prepared, the organic halide is introduced into the reaction tube as described. After evaporating the solvent the reaction tube is detached and weighed and the contents are treated by various means, depending upon the nature of the product.

## III. Actions of Sodium Triphenyl Germanide on Methyl Iodide and Ethyl Bromide

**Methyl Iodide.**—Reaction takes place according to the equation

$$CH_3I + NaGe(C_6H_5)_3 = NaI + CH_3Ge(C_6H_5)_3 \quad (I)$$

After preparing the solution of sodium triphenyl germanide in liquid ammonia, methyl iodide, in excess, was added through the addition tube 2b as described above. Reaction took place immediately with the formation of a voluminous white precipitate which slowly settled and agglomerated to a granular mass. The ammonia was then evaporated and the last traces removed by means of a pump. The dry white powder which remained was transferred to an extraction funnel and extracted with benzene. On evaporating the benzene under diminished pressure, colorless transparent crystals remained which, after washing with low-boiling petroleum ether, melted at 69–70°. Neglecting material contained in the washings, a yield of 86% was obtained. The compound was crystallized by dissolving in chloroform and precipitating with methyl alcohol.

Analysis for germanium was carried out by oxidizing with fuming sulfuric and nitric acids according to the method commonly used in this Laboratory.[7]

*Anal.* Subs., 0.2591, 0.1903, 0.1693: $GeO_2$, 0.0860, 0.0621, 0.0557. Calcd. for $(C_6H_5)_3GeCH_3$: Ge, 22.78. Found: Ge, 22.99, 22.65, 22.83, mean, 22.82.

The molecular weight of the compound was determined in benzene by the cryoscopic method.

*Mol. wt.* Solvent, 21.91; solute 0.1851, 0.3272; $\Delta t$, 0.142, 0.252°; mol. wt. calcd. for $(C_6H_5)_3GeCH_3$, 318.7; found: 304, 305.

Triphenylmethylgermane is very soluble in benzene, ether, petroleum ether, acetone and chloroform. It is slightly soluble in isopropyl alcohol and almost insoluble in cold methyl alcohol. It is quite insoluble in liquid ammonia. It melts at 70.5–71.0°. It does not react with sodium in liquid ammonia.

**Ethyl Bromide.**—Reaction takes place according to the equation

$$(C_6H_5)_3GeNa + C_2H_5Br = (C_6H_5)_3GeC_2H_5 + NaBr \qquad (II)$$

Triphenylethylgermane has been prepared previously by Orndorff, Tabern and Dennis[8] by the action of ethylmagnesium bromide on triphenylgermanium bromide.

Ethyl bromide reacts readily and quantitatively with sodium triphenyl germanide, the reaction being carried out as already described in connection with methyl iodide. The compound was recrystallized from isopropyl alcohol and melted at 78–78.5°, which is slightly higher than that recorded by Orndorff, Tabern and Dennis.

*Anal.* Subs., 0.2124, 0.2186: $GeO_2$, 0.0671, 0.0692. Calcd. for $(C_6H_5)_3GeC_2H_5$: Ge, 21.82. Found: Ge, 21.88, 21.97, mean, 21.92.

The molecular weight was determined in benzene solution by the cryoscopic method.

*Mol. wt.* Solvent, 19.75; solute, 0.2174, 0.4587, 0.5582; $\Delta t$, 0.174, 0.375, 0.456°; mol. wt. calcd. for $(C_6H_5)_3GeC_2H_5$, 332.7. Found, 324, 317, 317, mean, 319.

Triphenylethylgermane is very soluble in ether, petroleum ether, benzene, chloroform, acetone and trichloroethylene. It is slightly soluble in isopropyl acohol and almost insoluble in methyl alcohol; it melts at 78–78.5°.

Triphenylethylgermane reacts readily with bromine, apparently with the substitution of a phenyl group. On carrying out such bromination in carbon tetrachloride, a product was obtained that melted at 67–70°. It contained bromine and sublimed readily at 100° in vacuum. Had the ethyl group been substituted, the resulting triphenylgermanium bromide would have melted at 138°.

## IV. Action of Sodium Triphenyl Germanide on Methylene Chloride

It might be expected that the reaction between sodium triphenylgermanide and methylene chloride would take place according to the equation

$$2(C_6H_5)_3GeNa + CH_2Cl_2 = [(C_6H_5)_3Ge]_2CH_2 + 2NaCl \qquad (III)$$

The corresponding reaction has been shown to take place in the case of sodium triphenyl stannide[4] as well as sodium trimethyl stannide.[2]

When methylene chloride or bromide is added to a solution of sodium triphenyl germanide in liquid ammonia, reaction takes place in the main according to equation III. However, a side reaction occurs, inasmuch as there are recovered, along with di-triphenylgermanylmethane, smaller

[7] Kraus and Brown, THIS JOURNAL, **52**, 3693 (1930).

[8] Orndorff, Tabern and Dennis, *ibid.*, **47**, 2039 (1925).

quantities of triphenylmethylgermane and triphenylgermanium oxide. The latter compound is a secondary product resulting from the hydrolysis of triphenylgermanyl amine, $(C_6H_5)_3GeNH_2$.

It may be pointed out that a reaction such as III is an ionic one and involves mutual oxidation and reduction between several of the molecular species. In ionic form the reaction would be written as follows

$$2(C_6H_5)_3Ge^- + CH_2Cl_2 = [(C_6H_5)_3Ge]_2CH_2 + 2Cl^-$$

The sodium ion takes no actual part in the reaction. What happens is that chlorine, being much more electronegative than germanium, takes over the electrons from the germanium ions to form chloride ions, while the germanium groups combine with the residual carbon valences.

Owing to the affinity of germanium for nitrogen on the one hand and the affinity of carbon for hydrogen on the other, reactions may occur in which ammonia is concerned, the amino group of the ammonia combining with germanium and the hydrogen combining with carbon. In the case of simple carbon groups, as, for example, methyl or ethyl groups, the germanium is coupled quantitatively to carbon. When, however, we come to the more highly halogenated carbon derivatives, only one of the halogens is substituted quantitatively by the germanyl group, while the others are substituted only incompletely. The reaction of sodium triphenyl germanide with methylene chloride in liquid ammonia may be formulated as follows

$$2(C_6H_5)_3Ge^- + CH_2Cl_2 \longrightarrow [(C_6H_5)_3Ge]_2CH_2 + 2Cl^- \quad \text{(IVa)}$$

$$2(C_6H_5)_3Ge^- + CH_2Cl_2 + NH_3 \longrightarrow (C_6H_5)_3GeNH_2 + (C_6H_5)_3GeCH_3 + 2Cl^- \quad \text{(IVb)}$$

In the case of methylene chloride and bromide, reaction takes place in the main according to equation IVa. Comparatively small amounts of triphenylmethylgermane and triphenylgermanylamine are formed. The proportion of reaction IVb seemed to be somewhat greater in the case of methylene chloride than in that of methylene bromide. In the reactions as carried out, triphenylgermanylamine was not recovered as such, since the reaction products were handled in the atmosphere and, as Wooster has shown, the amine is completely hydrolyzed under these conditions.[9] The corresponding oxide, however, was recovered in all cases.

While reaction IVb is not of any considerable consequence in the case of methylene chloride, it becomes of great importance in the case of chloroform, as will be described in the next section.

In carrying out the reaction between sodium triphenyl germanide and methylene halide, the method was much the same as that described in the preceding section except that the methylene chloride was introduced by means of ammonia vapor passing over the liquid contained in tube H. The reaction with methylene chloride and bromide takes place immediately, a white, curdy precipitate being formed. After evaporating the solvent and pumping off the ammonia, a pasty mass remained which was converted to a dry white powder on exposure to the air. On extracting the organic materials with

[9] Kraus and Wooster, THIS JOURNAL, **52**, 372 (1930).

benzene and subjecting the resulting product to sublimation at 100° under a pressure of 0.05 mm., about 20% of the material was obtained as a sublimate, melting at 70–71°. In three cryoscopic determinations of the molecular weight in benzene, the values 328.6, 327.3 and 318.6 were obtained, which corresponds closely with the molecular weight of triphenylmethylgermane, 318.7. The melting point of a mixture of this sublimate with known triphenylmethylgermane served to identify it definitely as the latter compound.

**Di-triphenylgermanylmethane.**—The main portion of the reaction product remained after the sublimation at lower pressures at a temperature of 100°. This residue was found to melt, for the most part, at 143–147°, although some remained solid up to 160°. A great deal of difficulty was experienced in purifying this material, which might have been expected to be a nearly pure substance. The melting point varied from 139 to 180°. Finally, by careful fractional crystallization from a mixture of chloroform and methyl alcohol, two substances were separated. The one had a melting point of 180–182° and was shown to be triphenylgermanium oxide, while the other had a melting point of approximately 139°. By recrystallization, large, transparent, prismatic crystals were obtained from the 139° product which melted at 134.5°, and, on further purification, a few crystals were obtained that melted at 132–133°. The lower-melting crystals were identified as di-triphenylgermanylmethane.

*Anal.* Subs., 0.2410, 0.4814: $GeO_2$, 0.0806, 0.1617. Calcd. for $[(C_6H_5)_3Ge]_2CH_2$: 23.36. Found: Ge, 23.20, 23.31, mean, 23.26.

The molecular weight of the compound was determined in benzene by the cryoscopic method.

*Mol. wt.* Solvent, 18.77; solute, 0.1731, 0.2471, 0.3183; $\Delta t$, 0.073, 0.105, 0.142°; mol. wt. calcd. for $[(C_6H_5)_3Ge]_2CH_2$: 621.4; found: 647, 642, 611, mean, 633.

Di-triphenylgermanylmethane is very soluble in ether, petroleum ether, benzene, chloroform and trichloroethylene. It is quite insoluble in liquid ammonia and the lower acohols. It forms large transparent prisms when allowed to crystallize slowly from a chloroform–methyl alcohol mixture.

Di-triphenylgermanylmethane forms a series of solid solutions with triphenylgermanium oxide from which it is separated with difficulty. The existence of these solid solutions was shown by taking the melting point of known mixture. With di-triphenylgermanyl methane melting at 134° and triphenylgermanium oxide melting at 183°, mixtures were made up in the ratios of 3.4:1, 1:1, and 1:2. These melted, respectively, in the ranges 135–160, 145–170 and 170–181°. The two compounds appear to be miscible in all proportions and with rather slight difference between the composition of the liquid and solid phases.

## V. Action of Sodium Triphenyl Germanide on Chloroform

While one might expect that, on treating chloroform with sodium triphenyl germanide, an appreciable amount of the tertiary substituted methane would be produced, there were actually obtained the same products as in the methylene chloride reaction. The proportion of di-triphenylgermanylmethane and of triphenylgermanylamine was, however, much greater than in the case of methylene chloride. A relatively small amount of triphenylmethylgermane is also formed.

It is evident that of the three chlorine atoms attached to carbon in chloroform, one is quantitatively substituted by a triphenylgermanyl group; a second halogen atom is largely substituted while the third is completely replaced by hydrogen. The reactions may be formulated as follows

$$3(C_6H_5)_3Ge^- + CHCl_3 + NH_3 = [(C_6H_5)_3Ge]_2CH_2 + (C_6H_5)_3GeNH_2 + 3Cl^- \quad (Va)$$
$$3(C_6H_5)_3Ge^- + CHCl_3 + 2NH_3 = (C_6H_5)_3GeCH_3 + 2(C_6H_5)_3GeNH_2 + 3Cl^- \quad (Vb)$$

For the most part, reaction takes place according to equation Va.

Several reactions were carried out in a two-legged reaction tube in which bromoform was added to the solution of sodium triphenyl germanide in liquid ammonia. After evaporating the ammonia, the material was treated with various dry solvents in the absence of air in order to separate the organic product from the sodium bromide formed in the reaction. There was evidence that two soluble organic products were formed, one of which melted at 60–70° and was undoubtedly triphenylmethylgermane, although this product was present in very small amount. The reaction was finally carried out with the apparatus shown in Fig. 1, passing the chloroform into the reaction tube by means of ammonia vapor as already described.

A voluminous white precipitate resulted which resembled that formed in the methylene chloride reaction. It was slightly pasty when the ammonia was first evaporated but became dry upon standing in air. This was probably due to the conversion of triphenylgermanylamine to oxide by hydrolysis. On recrystallization, the product showed the same properties as did that of the methylene chloride reaction. The melting point varied with the treatment and extended over a considerable temperature range. After several recrystallizations from chloroform–alcohol mixtures, a product was separated that melted at 139–141°. Molecular weight determinations with this product in benzene by the cryoscopic method yielded the values 551 and 565, respectively; the molecular weight of di-triphenylgermanylmethane is 621.5 and that of tri-triphenylgermanylmethane is 924.2. The molecular weight indicated that tertiary substitution does not occur in the case of chloroform. An analysis of the product melting at 139° showed 23.57% of germanium as against 23.57% required for the tertiary derivative, and 23.36 for the di-substitution product. The composition of the two compounds is so nearly the same that analysis cannot be depended upon in distinguishing between them. The molecular weight, however, gives conclusive results.

By repeated recrystallization of the 139° product, crystals were finally obtained that melted at 132–134°. On comparing the melting point of this compound with that of known di-triphenylgermanylmethane and mixtures of the two, it was established that the 132–134° product was, in fact, di-triphenylgermanylmethane.

In the case of the methylene chloride reaction, a small quantity of a higher melting material was obtained which was identified as triphenylgermanium oxide by comparison of its melting point with that of known oxide and of mixtures of the two. In the chloroform reaction, relatively greater quantities of the same material were obtained and were similarly identified as triphenylgermanium oxide. As a further check on the identity of this material, it was treated with aqueous hydrobromic acid and petroleum ether. After removing the ether, the product was sublimed in a vacuum at 150°. The sublimate melted at 135–136°, which corresponds to the melting point of impure triphenylgermanium bromide. The high melting product is triphenylgermanium oxide which results from the hydrolysis of triphenylgermanylamine due to the moisture present in the atmosphere and in the solvents used in recrystallization.

## VI. Action of Sodium Triphenyl Germanide on Carbon Tetrachloride

It might be expected that on treating carbon tetrachloride with sodium triphenyl germanide a quaternary substituted carbon compound would result. On the other hand, since the tertiary substituted product is not formed in the case of chloroform, the quaternary product is scarcely to be

expected in the case of carbon tetrachloride. Foster[10] carried out a reaction between sodium triphenyl germanide and carbon tetrachloride in benzene solution and found that hexaphenylgermanoethane was formed, together with a small amount of triphenylgermanium oxide. He did not study the reaction in detail and did not determine what becomes of the carbon atom of the original tetrachloride.

When carbon tetrachloride was treated with sodium triphenyl germanide in liquid ammonia solution, a pasty mass was obtained. On extracting with benzene and evaporating the solvent, crystals were obtained along with adhering liquid material. After washing with petroleum ether, the residue was found to melt at 156–160°. This material was recrystallized from chloroform–methyl alcohol solution and from petroleum ether, which raised the melting point to 178–179°. By comparison with known triphenylgermanium oxide, the compound was identified as this oxide.

From the petroleum ether washings, various crystalline products were obtained melting at 139–150, 63–69, 88–95 and 91–93°. The quantities were not sufficient for purification and identification. They probably comprised some triphenylmethylgermane and di-triphenylgermanylmethane.

When sodium triphenyl germanide reacts with carbon tetrachloride in liquid ammonia, no triphenylgermanium results. The large amount of triphenylgermanium oxide formed indicates that a large part of the germanium is converted to triphenylgermanylamine, corresponding to which the carbon atom must have been hydrogenated. The low-melting products doubtless contain this hydrogen.

The results of the present investigation illustrate the propensity of the lighter elements of the fourth group to combine with nitrogen. This tendency appears again and again in the case of various reactions in which organic germanium derivatives are involved and to a still greater extent in the case of silicon, as will be shown in subsequent papers.

## Summary

The reaction of sodium triphenyl germanide with various organic halides in liquid ammonia has been studied. The monohalogen derivatives react quantitatively according to the equation

$$(C_6H_5)_3GeNa + RX = NaX + (C_6H_5)_3GeR$$

In the case of methylene chloride, the final products obtained are triphenylgermanylmethane, triphenylgermanium oxide and di-triphenylgermanylmethane. The last-named compound is the normal substitution product due to reaction of the two chlorine atoms of methylene chloride with the weakly negative ions of sodium triphenyl germanide. The other two compounds are due to the fact that one of the carbon valences reacts with ammonia. A hydrogen atom of ammonia combines with one of the carbon valences while the remaining amino group combines with the triphenylgermanium group. The resulting triphenylgermanylamine is hydrolyzed to oxide in the course of separation. The reaction as it takes place in liquid ammonia is as follows

$$2(C_6H_5)_3GeNa + H_2CCl_2 + NH_3 = 2NaCl + (C_6H_5)_3GeCH_3 + (C_6H_5)_3GeNH_2$$

[10] Foster, Thesis, Brown University, 1927.

In the reaction between sodium triphenyl germanide and chloroform, the products are the same as in that with methylene chloride, but the proportion in which the compounds are formed is different. Larger quantities of triphenylgermanylamine (ultimately recovered as oxide) are obtained while the amount of triphenyl methyl germane is relatively smaller. Very considerable quantities of di-triphenylgermanylmethane are formed.

Di-triphenylgermanylmethane and triphenylgermanium oxide form a series of solid solutions that may be separated with some difficulty.

Sodium triphenyl germanide reacts readily with carbon tetrachloride. The reaction is evidently similar to that with chloroform and methylene chloride although apparently more complex. No free triphenylgermanium is formed. Triphenylgermanium oxide was obtained from the reaction mixture as well as a number of lower melting compounds that have not been separated and identified. Without doubt, ammonia takes part in this reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

# *l*-*p*-METHOXYPHENYLALANINE[1]

BY LETHA DAVIES BEHR AND H. T. CLARKE

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The methyl ether of racemic tyrosine has been prepared, by purely synthetic methods, by Dakin.[2] Need having arisen for an optically active variety of this acid, its preparation from natural tyrosine was indicated. The action of diazomethane upon tyrosine has been shown[3] to lead to a mixture of methyl esters which includes that of methoxyphenylalanine, but the process is obviously unsuitable for preparative purposes.

Methylation by means of methyl sulfate has proved eminently satisfactory, protection of the amino group being secured by acetylation. For this purpose it is desirable to select conditions in which only the amino group is acetylated, the phenolic hydroxyl group remaining intact. It has recently been shown that, in general, both the amino group and the phenolic hydroxyl group are readily acetylated by treatment in cold alkaline solution with acetic anhydride[4] or with ketene;[5] the hydroxyl group of tyrosine

[1] Work supported by a research grant from the Chemical Foundation.

[2] H. D. Dakin, *J. Biol. Chem.*, **8**, 11 (1910); A. J. Wakeman and H. D. Dakin, *ibid.*, **9**, 148 (1911).

[3] E. Abderhalden and E. Schwab, *Z. physiol. Chem.*, **148**, 16 (1925).

[4] F. D. Chattaway, *J. Chem. Soc.*, 2495 (1931); C. P. Berg, W. C. Rose and C. S. Marvel, *J. Biol. Chem.*, **85**, 207 (1929).

[5] M. Bergmann, and F. Stern, *Ber.*, **63B**, 437 (1930).

would also be acetylated by heating with acetic anhydride alone,[6] or in glacial acetic acid,[7,8] while in pyridine abnormal reactions take place.[9]

We have found that tyrosine may be acetylated readily on the nitrogen alone by addition of acetic anhydride to its suspension in hot water. The resulting product is apparently soluble in all proportions in water and was obtained in the form of an almost colorless glass, which nevertheless gave analytical figures corresponding approximately to those of monoacetyltyrosine. Only about 10% of the tyrosine was racemized during the process. Monoacetyl-*l*-tyrosine has been prepared by Takenaka[10] from tyrosine ethyl ester by acetylating with acetic anhydride and saponifying with alkali; his product is reported to crystallize with difficulty from water and to melt at 146–148°. We have not succeeded in crystallizing from water the monoacetyltyrosine prepared as above, but have isolated from dioxane solution a crystalline product containing one molecule of solvent. The dioxane of crystallization is not completely lost on heating at 76° for forty-eight hours *in vacuo* over phosphorus pentoxide; at 120–125° the anticipated loss of weight takes place after a week, but some decomposition of the acetyltyrosine also occurs.

On treatment in alkaline solution with methyl sulfate, monoacetyltyrosine readily yields N-acetyl-*p*-methoxyphenylalanine, which on hydrolysis with dilute mineral acid is converted to the desired *l-p*-methoxyphenylalanine.

The optically active acid melts at a distinctly lower temperature than the racemic modification; its solubility in water is markedly greater than that of tyrosine, and it is interesting to note that its levorotation, in contradistinction to that of tyrosine, is lower in sodium hydroxide than in hydrochloric acid:

| | $[\alpha]_{546}$ in *N* HCl | $[\alpha]_{546}$ in *N* NaOH |
|---|---|---|
| *l*-Tyrosine | −11.7° | −14.6° |
| *l-p*-Methoxyphenylalanine | − 5.9 | − 3.2 |

The specific rotatory power of its derivatives varies within wide limits, from weakly levo (−3.7° for the benzoyl derivative) to strongly dextro (+123.6° for the phenylhydantoic acid).

## Experimental

*l*-N-**Acetyltyrosine.**—To a suspension of 90.5 g. of tyrosine in 500 cc. of water at 90–95° was added 375 cc. of 95% acetic anhydride in eight portions, any ebullition having been allowed to subside before each new addition. The tyrosine was completely in solution after 325 cc. had been added. The resulting solution was evaporated on the steam-bath under reduced pressure until no further acetic acid distilled. The sirupy, pale

[6] P. A. Levene and R. E. Steiger, *J. Biol. Chem.*, **93**, 581 (1931).
[7] F. Knoop and J. G. Blanco, *Z. physiol. Chem.*, **146**, 267 (1925).
[8] H. D. Dakin, *J. Biol. Chem.*, **82**, 439 (1929).
[9] H. D. Dakin and R. West, *ibid.*, **78**, 91, 744 (1928).
[10] Y. Takenaka, *Acta Schol. Med. Univ. Imp. Kioto*, **4**, 367 (1922).

yellow residue was dissolved in acetone, filtered from a small quantity of unchanged tyrosine, evaporated, and dried at 75° *in vacuo* over potassium hydroxide and phosphorus pentoxide.

*Anal.* Calcd. for $C_{11}H_{13}O_4N$: C, 59.19; H, 5.83; N, 6.28; neut. equiv., 223. Found: C, 58.98, 58.92; H, 5.41, 5.65; N, 5.67; neut. equiv. (phenolphthalein), 227.

*Rotation.* $[\alpha]^{22}_{546}$ +46.2° (4.4% in water), +84.4° (3.7% in *N* NaOH, +39.8°) (2.9% in *N* HCl).

In order to estimate the extent of racemization which takes place during the acetylation, 5 g. of tyrosine was treated as above and the product hydrolyzed by boiling for four hours with 60 cc. of 1.7 *N* hydrochloric acid. On neutralization with ammonia, 5 g. of tyrosine was recovered, showing $[\alpha]^{23}_{546}$ −9.9°. On recrystallizing 3.8 g. of this recovered tyrosine from 700 cc. of water, 2.8 g. of tyrosine, showing $[\alpha]^{21}_{546}$ −12.0° (4% in *N* HCl), was obtained. Concentration of the mother liquors yielded further crops showing considerably lower rotations.

On dissolving the resinous acetyltyrosine in the minimum quantity of cold dioxane and adding an equal volume of petroleum ether, the product separated as an oil which became crystalline on standing overnight in the refrigerator. On recrystallization from hot dioxane, it separated in irregular plates which, after drying at room temperature under reduced pressure over phosphorus pentoxide, melted at 107–109° after softening at about 98°. The molten product resolidified on cooling and on heating again melted (not very sharply) at 138–140°.

*Anal.* Calcd. for $C_{15}H_{21}O_6N$: C, 57.88; H, 6.75; N, 4.50; neut. equiv., 311. Found: C, 57.63; H, 6.67; N, 4.43; neut. equiv. (phenolphthalein), 318.

*Rotation.* $[\alpha]^{22}_{546}$ +39.9° (4.2% in water), +72.3° (3.3% in *N* NaOH), +33.8° (2.8% in *N* HCl).

A sample, heated for forty-eight hours at 76° *in vacuo* over phosphorus pentoxide, lost 19% of its weight (calcd., 28.3%). After heating for a week longer at 120–125° loss of weight increased to 28.4%, but decomposition occurred at this temperature as indicated by darkening and formation of some water-insoluble resin. Analysis of the material so heated gave C, 59.50; H, 5.98; N, 5.84.

**Methylation.**—The sirupy residue from the acetylation of 90.5 g. of tyrosine was dissolved in 400 cc. of water; the solution was neutralized with barium carbonate and then rendered alkaline by the addition of 189.3 g. of hydrated barium hydroxide. To the resulting mixture was added, with mechanical stirring, 126 g. of methyl sulfate in four portions, the temperature being held at 30–40° by external cooling. Stirring was continued for two hours after all of the methyl sulfate had been added. The solution was filtered to remove a little undissolved barium hydroxide and added to a boiling solution of 100 g. of concentrated sulfuric acid in 500 cc. of water. On allowing to cool and filtering off the barium sulfate, a part of the acetyl-*p*-methoxyphenylalanine separated as an oil. A portion was allowed to stand in the refrigerator, when it gradually crystallized. The crude product, which melted at 145°, was recrystallized from water, when it was obtained in either trapezoidal plates or hard blunt needles which melted at 150–151°. *l*-N-Acetyl-*p*-methoxyphenylalanine is extremely soluble in methyl alcohol, ethyl alcohol and acetone, sparingly soluble in cold water, and insoluble in ether.

*Anal.* Calcd. for $C_{12}H_{15}O_4N$: C, 60.76; H, 6.33; N, 5.91. Found: C, 61.14; H, 6.40; N, 6.02.

*Rotation.* $[\alpha]^{20.5}_{546}$ +67.6° (5% in absolute alcohol). $[\alpha]^{24}_{546}$ +78.4 (4.5% in *N* NaOH).

***l*-*p*-Methoxyphenylalanine.**—The crude solution containing the *l*-N-acetyl-*p*-methoxyphenylalanine (obtained as above from 90.5 g. of tyrosine), which was strongly

acid to Congo red, was heated for seventy-two hours on the steam-bath and then evaporated almost to dryness on the steam-bath under reduced pressure. The residue on cooling solidified to a crystalline mass. This was washed with cold glacial acetic acid until free of color, and then with acetone until free of acetic acid. The product so obtained, after drying *in vacuo* over phosphorus pentoxide, weighed 81.5 g. and melted at 188–189° (corr.). A second crop of 17.8 g., melting at 187–188° (corr.), was obtained by repeating the evaporation and washing. An attempt to obtain a third crop in this way yielded only 0.2 g. of reddish crystals, but a further crop, amounting to about 10 g., was obtained from the mother liquor by partially removing the excess sulfuric acid with barium hydroxide and again concentrating. The crude material was recrystallized by dissolving in hot water, decolorizing with charcoal, concentrating on the steam-bath until a coating of crystals formed on the surface, diluting with 50 cc. of acetic acid and cooling. On washing successively with acetic acid and acetone, and drying *in vacuo* over phosphorus pentoxide, it melted at 191° (corr.). Analysis showed it to consist of the acid sulfate of *p*-methoxyphenylalanine.

*Anal.* Calcd. for $C_{10}H_{13}O_3N \cdot H_2SO_4$: S, 10.92; N, 4.78. Found: S, 10.66; N, 4.92.

The final yield, after working up the mother liquors, was 99 g., or 68% of the theoretical amount based on the 90.5 g. of tyrosine originally taken. The salt is exceedingly soluble in water and in ethyl alcohol, sparingly soluble in acetic acid, and insoluble in acetone.

The free *p*-methoxyphenylalanine was readily obtained by adding a slight excess of ammonia to a hot aqueous solution of the acid sulfate, when it crystallized as glistening plates which melted at 264–265° (corr.).

*Anal.* Calcd. for $C_{10}H_{13}O_3N$: C, 61.54; H, 6.67; N, 7.18; $CH_3O$, 15.90. Found: C, 61.65; H, 6.35; N, 7.24; $CH_3O$, 15.62.

*Rotation.* $[\alpha]_{546}^{29}$ −5.9° (2% in *N* HCl), −3.2° (2% in *N* NaOH).

*l*-*p*-Methoxyphenylalanine dissolves in 101–102 parts of water at 25° and in about 18 parts at 100°. When the aqueous solution is boiled in the presence of air, decomposition gradually occurs; the solution becomes slightly turbid, traces of carbon dioxide and ammonia are evolved, and an odor recalling that of anisaldehyde is perceptible. Tyrosine, to a less extent, displays a similar tendency to lose carbon dioxide and ammonia.

The hydrochloride crystallizes readily from hydrochloric acid solution in the form of stout needles which melt at 237–238° (corr.) with evolution of gas. It is readily soluble in water and absolute alcohol but insoluble in ether.

*Anal.* Calcd. for $C_{10}H_{14}O_3NCl$: Cl, 15.33; N, 6.05. Found: Cl, 15.38; N, 6.30.

The copper salt forms sparingly soluble violet-blue leaflets which, on rapid heating, decompose at 250° (corr.).

*Anal.* Calcd. for $C_{20}H_{24}O_6N_2Cu$: Cu, 14.08. Found: Cu, 14.03, 14.01.

Attempts to prepare a crystalline picrate were unsuccessful; the amorphous salt was relatively soluble in water and in alcohol. The picrolonate separated from 30% alcohol in rosets of fine needles which softened at 145° and melted with decomposition at 174° (corr.). Recrystallization of this salt failed to change these characteristics and the product continued to give unsatisfactory analytical values.

*Anal.* Calcd. for $C_{10}H_{13}O_3N \cdot C_{10}H_8O_5N_4$: C, 52.29; H, 4.58; N, 15.25. Found: C, 51.80; H, 5.13; N, 12.42.

**Benzoyl Derivative.**—This was prepared by the Schotten–Baumann reaction in the presence of sodium bicarbonate. It formed very fine needles which, after recrystallization from water, melted at 136–137°; it is soluble in alcohol, insoluble in benzene.

*Anal.* Calcd. for $C_{17}H_{17}O_4N$: N, 4.68. Found: N, 4.81.
*Rotation.* $[\alpha]^{20}_{546}$ −3.7° (1.5% in alcohol).

**Benzenesulfonyl Derivative.**—This was prepared by the Schotten–Baumann procedure in the presence of sodium bicarbonate; it separated from hot water in long fine needles which melted at 136–137°.

*Anal.* Calcd. for $C_{16}H_{17}O_5NS$: S, 9.55. Found: S, 9.37.
*Rotation.* $[\alpha]^{21}_{546}$ +6.3° (1% in alcohol).

An alkali-insoluble oil which accompanied this product was not investigated.

**Phenylhydantoic Acid.**—A solution of 2 g. of *l*-*p*-methoxyphenylalanine in 42 cc. of 0.43 *N* sodium hydroxide was shaken with 3 cc. of phenyl isocyanate for an hour. After filtering, the alkaline solution was acidified to Congo red, and the crude product was recrystallized from 50 cc. of 50% alcohol, from which it separated as glistening leaflets melting at 176–177° (corr.). Another preparation was recrystallized from ethylene chloride, in which it is very sparingly soluble in the cold.

*Anal.* Calcd. for $C_{17}H_{18}O_4N_2$: C, 64.97; H, 5.73; N, 8.92. Found: C, 64.78; H, 5.85; N, 8.99.
*Rotation.* $[\alpha]^{21}_{546}$ +123.6° (4% in alcohol).

**Phenylhydantoin.**—A solution of 1 g. of the above phenylhydantoic acid in 150 cc. of 10% hydrochloric acid was boiled for one and one-half hours. The hot solution was filtered; on cooling, the phenylhydantoin separated in fine needles which melted at 134–135°. This melting point was unchanged on recrystallization from water.

*Anal.* Calcd. for $C_{17}H_{16}O_3N_2$: C, 68.92; H, 5.41; N, 9.46. Found: C, 69.13; H, 5.52; N, 9.53.

**α-Naphthylhydantoic Acid.**—This was prepared in the same way as the phenyl derivative from 2 g. of the amino acid and 3 cc. of α-naphthyl isocyanate. The alkaline solution had to be heated before the dinaphthyl urea could be filtered off. On recrystallization from 50% alcohol, the derivative separated in the form of small prisms which melted at 167–168°.

*Anal.* Calcd. for $C_{21}H_{20}O_4N_2$: C, 69.23; H, 5.49; N, 7.69. Found: C, 69.38; H, 5.65; N, 7.83.
*Rotation.* $[\alpha]^{22}_{546}$ +63.3° (2.5% in alcohol).

**α-Naphthylhydantoin.**—The above α-naphthylhydantoic acid underwent very little change on heating for two hours with 80 parts of 10% hydrochloric acid, probably owing to lack of solubility. The conversion was brought about by heating 0.4 g. with a mixture of 100 cc. of water, 25 cc. of glacial acetic acid, and 40 cc. of concentrated hydrochloric acid. After two hours' boiling, the mixture was filtered hot and the amorphous precipitate which separated from the filtrate was recrystallized from 25% alcohol; it formed short prisms melting at 155–157°.

*Anal.* Calcd. for $C_{21}H_{18}O_3N_2$: C, 72.83; H, 5.20; N, 8.09. Found: C, 72.76; H, 5.25; N, 8.34.

The authors desire to express their indebtedness to Mr. W. Saschek, who carried out the microanalyses here reported.

## Summary

A synthesis of *l*-*p*-methoxyphenylalanine from *l*-tyrosine is described, and the product is characterized by various derivatives.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

# ALIPHATIC GERMANIUM DERIVATIVES. I. TRIETHYLGERMANIUM COMPOUNDS; SOME OF THEIR PROPERTIES AND REACTIONS

BY CHARLES A. KRAUS AND E. ALISON FLOOD

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## I. Introduction

When three of the valences of the fourth group elements are satisfied by hydrogen or, more frequently, hydrocarbon radicals, they form groups of the type $R_3A$ which in many respects resemble corresponding derivatives of carbon. In the case of tin, for example, the tertiary alkyl and aryl derivatives resemble the corresponding derivatives of triphenylmethyl in many respects. The corresponding silicon derivatives resemble triphenylmethyl less closely than do those of tin for the reason that the Si–Si linkage is much more stable than the Sn–Sn linkage, while the halogen derivatives of the type $R_3SiX$ have a great tendency to hydrolyze.

The triphenylgermanium and the diphenylgermanium groups and some of their derivatives have previously been investigated[1] in this Laboratory. In the present paper are presented the results of a study of the triethylgermanium group and its derivatives. Since these derivatives have not heretofore been prepared, much of the present investigation is necessarily concerned with the preparation of compounds and the examination of some of their properties.

## II. Triethylgermanium Halides and Di-triethylgermanium Oxide Tetraethylgermane

**Preparation.**—Triethylgermanium bromide, which serves as starting material in the preparation of triethylgermanium derivatives, may be prepared either by the partial ethylation of germanium tetrabromide by means of the Grignard reagent or by the substitution of one of the ethyl groups of tetraethylgermane by bromine. While we have found that triethylgermanium bromide may be prepared by the first method, the yields were not favorable. On the other hand, with suitable precautions, triethylgermanium bromide may be prepared from tetraethylgermanium by direct bromination with good yields.

Tetraethylgermanium was first prepared by Winkler,[2] using zinc ethyl as ethylating agent and more recently by Tabern, Orndorff and Dennis[3] by means of the Grignard reagent. The latter authors report a yield of

[1] Kraus and Foster, THIS JOURNAL, **49**, 457 (1927); Kraus and Wooster, *ibid.*, **52**, 372 (1930); Kraus and Brown, *ibid.*, **52**, 3690, 4031 (1930).

[2] Winkler, *J. prakt. Chem.*, **144** (N. F. **36**), 177 (1887).

[3] Tabern, Orndorff and Dennis, THIS JOURNAL, **47**, 2039 (1925).

60%. Using suitable precautions, we have found that tetraethylgermane may be prepared by the action of ethylmagnesium bromide on germanium tetrabromide with practically quantitative yield. In view of the high cost of germanium, we describe the method here.

A solution of 130 g. of germanium tetrabromide in ether was slowly added to a solution of ethylmagnesium bromide made up from 222 g. of ethyl bromide in 300 cc. of ether. During this process, the reaction mixture was strongly cooled and vigorously stirred by means of a motor-driven, mercury-sealed stirrer, an atmosphere of nitrogen being maintained over the reaction mixture. The mixture was boiled for two hours and allowed to stand overnight, when it was found to have separated into two layers. The ether was distilled from the mixture through a fractionating column, the mixture being stirred during the process. When most of the ether had been removed, a colorless solid separated from solution. At this juncture, care was taken to keep the mixture thoroughly stirred and uniformly heated. Finally, after removal of the uncombined ether, stirring was interrupted and the reaction mixture was heated to 110° for eight hours. The mixture was then cooled and ether was again added, the two liquid layers being reformed. The mixture was now chilled in an ice-bath, the excess Grignard reagent was destroyed and the product of reaction was extracted with ether. After drying, the ether, solution was distilled through a fractionating column. The higher boiling product was again distilled under reduced pressure. Three fractions were collected, a middle fraction of 56.7 g., boiling at 163.5° (uncorr.), and a higher and a lower boiling fraction of 3 g. each, which consisted chiefly of tetraethylgermane. Not counting these fractions, the yield was 91%.

The more common physical and chemical properties of germanium tetraethyl have been reported by Winkler, and more recently and completely by Dennis and Hance.[4] Germanium tetraethyl is practically insoluble in liquid ammonia and perhaps for this reason does not react appreciably with a solution of sodium in liquid ammonia. It does not react with germanium tetrabromide to an appreciable extent at 100° although tin tetraethyl reacts readily with tin tetrachloride at room temperatures.[5] The reaction of germanium tetraethyl with bromine is described in the next paragraph.

## Triethylgermanium Bromide

**Bromination of Germanium Tetraethyl.**—Bromine reacts with germanium tetraethyl in solution in carbon tetrachloride, ethylene dibromide and ethyl bromide at higher temperatures. The rate of reaction and the purity of the product is greatly influenced by the nature of the solvent medium as well as by concentration. Ordinarily, a mixture of triethylgermanium bromide and higher bromides is obtained. We have found that, under suitable conditions, a high yield of relatively pure triethylgermanium bromide may be obtained by the action of bromine on tetraethylgermane in ethyl bromide.

Successive portions of a 50% solution of bromine in ethyl bromide were added to germanium tetraethyl during a period of six days, the mixture being maintained at a temperature of 40°. The total weight of bromine added was about 5% above that required for the replacement of one ethyl group. From 25 g. of germanium tetrabromide,

[4] Dennis and Hance, THIS JOURNAL, **47**, 270 (1925).

[5] Stafford, Thesis, Brown University, 1928; Kazeschkow, *Ber.*, **62**, 996 (1929).

26 g. of triethylgermanium bromide were obtained, boiling within a range of 2°, a yield of 82%.

The product could not be purified by repeated fractional distillations, but it was found possible to recrystallize the bromide from a petroleum ether solution at −50°. This method was employed in the initial preparations. Later it was found more advantageous to convert the bromide to the oxide, which is readily purified. The oxide was then reconverted to the desired halide. This method is described below.

**Analytical Procedure.**—Analyses for germanium were carried out by the method commonly employed in this Laboratory[6] which consists in oxidizing the compounds by means of boiling, fuming sulfuric and nitric acids. The ethylgermanium derivatives are oxidized less readily than are the corresponding phenyl derivatives. As the nitric acid is boiled away, a point is reached where the solution takes on a greenish-brown color. If the process of boiling is continued at this point, a brown deposit is formed on the walls of the tube and germanium is lost, probably because of a volatile product present at this stage of the reaction. Accordingly, when this point is reached, a few drops of nitric acid are again added, boiling is resumed, and this process is repeated until, on continued boiling, a clear yellow solution results. The acids may then be fumed off and the tube and contents weighed after ignition.

Halogens, excepting fluorine, were determined as the silver halides. Since the triethylgermanium halides hydrolyze with some difficulty, a weighed sample was introduced into an ampule (2 cm. × 10 cm.) to which was then added a solution of potassium hydroxide. The neck of the ampule was then sealed, the mixture shaken vigorously and allowed to stand for twenty-four hours. The ampule was then opened and the organic material was extracted with petroleum ether. The residual alkaline solution was removed and the halogen precipitated by means of silver nitrate in the usual manner.

*Anal.* Subs., 0.5406, 0.4078: $GeO_2$, 0.2367, 0.1786. Calcd. for $(C_2H_5)_3GeBr$: Ge, 30.30. Found: Ge, 30.39, 30.41, mean, 30.40. Subs., 0.3836, 0.5175: AgBr, 0.3010, 0.4072. Calcd. for $(C_2H_5)_3GeBr$: Br, 33.35. Found: Br, 33.39, 33.48, mean, 33.43.

**Properties.**—Triethylgermanium bromide is a colorless, mobile liquid having an irritating, pungent odor resembling that of trimethyl tin bromide. It boils at 190.9°[7] under a pressure of 760 mm. and freezes when cooled to −33°. It is soluble in ordinary organic solvents and in ethylamine. When triethylgermanium bromide is treated with water or, better, with alkaline aqueous solutions, it is hydrolyzed with the formation of ditriethylgermanium oxide. Hydrolysis, however, proceeds much less readily than it does with the corresponding compounds of silicon and it may be handled in air without appreciable change. In liquid ammonia, triethylgermanium bromide is appreciably ammonolyzed and by suitable means ammonolysis may be carried to completion, ditriethylgermaniumimine being formed.

## Di-triethylgermanium Oxide

**Preparation.**—Impure triethylgermanium bromide is hydrolyzed with an aqueous solution of potassium hydroxide. The mixture is extracted with petroleum ether, the extract is dried with anhydrous sodium sulfate and then fractionally distilled. The chief impurity is diethylgermanium oxide which results on hydrolysis of diethylgermanium dibromide which is present as impurity. The latter oxide has a very high boiling point and thus is readily separated from triethylgermanium oxide. On the basis of a given sample of impure bromide, a yield of 97% was obtained.

[6] Kraus and Brown, Ref. 1, 3693.

[7] The boiling points of pure liquids as cited were determined by means of a calibrated thermocouple. All other temperatures are uncorrected.

*Anal.* Subs., 0.2765, 0.3550: $GeO_2$, 0.1727, 0.2215. Calcd. for $[(C_2H_5)_3Ge]_2O$: Ge, 43.29. Found: Ge, 43.34, 43.31, mean, 43.32.

*Mol. wt.* (Cryoscopic method in benzene). Solvent, 17.94, 17.94, 15.55; solute, 0.3802, 0.9526, 0.6863; $\Delta t$, 0.325, 0.810, 0.686. Calcd. for $[(C_2H_5)_3Ge]_2O$: 335.4. Found: 326, 328, 324, mean, 326.

**Properties.**—Di-triethylgermanium oxide is a colorless liquid possessing a camphor-like odor, in which respect it resembles the corresponding silicon derivative. It boils at 253.9° under normal pressure and does not solidify at −50°. It is soluble in common organic solvents and in ethylamine, but is insoluble in water and in liquid ammonia. It is quite stable toward oxidation and may be heated to 250° in air without appreciable decomposition. When ignited, it burns readily with a smoky flame. Treated with concentrated aqueous solutions of the halogen acids, the oxide is converted to the corresponding triethylgermanium halide. The oxide reacts readily with lithium in ethylamine with the formation of a reddish colored solution and without evolution of gas. Presumably, reaction takes place according to the equation

$$[(C_2H_5)_3Ge]_2O + 2Li = LiGe(C_2H_5)_3 + LiOGe(C_2H_5)_3$$

On evaporating the amine, the lithium triethyl germanide ammonolyzes, triethylgermane being formed.

**Triethylgermanium Iodide.**—A quantity of di-triethylgermanium oxide was treated with hydriodic acid and allowed to stand overnight. The triethylgermanium iodide was then extracted with petroleum ether, the extract dried and fractionally distilled. The fraction collected at the practically constant temperature of 210° was finally redistilled *in vacuo*.

*Anal.* Subs., 0.5031, 0.4558: $GeO_2$, 0.1843, 0.1669. Calcd. for $(C_2H_5)_3GeI$: Ge, 25.33. Found: Ge, 25.43, 25.41, mean, 25.42. Subs., 0.3843, 0.3749: AgI, 0.3141, 0.3065. Calcd. for $(C_2H_5)_3GeI$: I, 44.28. Found: I, 44.18, 44.19, mean, 44.18.

**Properties.**—Triethylgermanium iodide is a colorless, mobile liquid possessing a peculiar, garlic-like odor. It boils at 212.3° under normal pressure. In other respects it resembles the bromide.

**Triethylgermanium Chloride.**—The preparation is precisely similar to that of the iodide except that hydrochloric acid is used in place of hydriodic acid.

*Anal.* Subs., 0.3265, 0.3676: $GeO_2$, 0.1755, 0.1981. Calcd. for $(C_2H_5)_3GeCl$: Ge, 37.20. Found: Ge, 37.31, 37.40, mean, 37.35. Subs., 0.1406, 0.1736: AgCl, 0.1038, 0.1281. Calcd. for $(C_2H_5)_3GeCl$: Cl, 18.17. Found: Cl, 18.26, 18.25, mean, 18.25.

**Properties.**—Triethylgermanium chloride is a colorless liquid boiling at 175.9° under normal pressure. It has a more penetrating odor than either the bromide or the iodide. In other respects it resembles the bromide although it appears to be somewhat less readily hydrolyzed.

## Triethylgermanium Fluoride

**Preparation.**—The preparation of the fluoride resembles that of the other halides except that the reaction is carried out in a lead vessel. The oxide is treated with hydrofluoric acid in a lead cylinder which is closed at one end and provided with a stopper at the other. The petroleum ether extract is dried with anhydrous sodium sulfate, since calcium chloride reacts with the fluoride.

Since hydrogen fluoride acts upon glass, the analysis of the compound for germanium had to be modified. The fluoride was oxidized in the usual way, the resulting oxide was dissolved in dilute sodium hydroxide and the germanium was precipitated as sulfide from 6 *N* acid solution. The sulfide was thrown on a filter, washed and trans-

ferred to a weighed crucible by washing with ammonium hydroxide. After expelling the ammonia and oxidizing the sulfide, the oxide was calcined and weighed.

*Anal.* Subs., 0.1608, 0.2233: $GeO_2$, 0.0940, 0.1308. Calcd. for $(C_2H_5)_3GeF$: Ge, 40.62. Found: Ge, 40.57, 40.65, mean, 40.61.

The fluorine was determined by two methods. The first was a modified Starcke method[8] in which the fluorine was weighed as lead chlorofluoride, while the second consisted in hydrolyzing the fluoride with a solution of known alkalinity and titrating the excess alkali with a standard solution of hydrochloric acid. Neither method proved to be entirely satisfactory, although the latter gave the more satisfactory results.

*Anal.* Subs., 0.3652, 0.3764: PbClF,[9] 0.5461, 0.4699. Calcd. for $(C_2H_5)_3GeF$: F, 10.24. Found: F, 10.86, 10.99, mean, 10.92. Subs., 0.4036, 0.2732: cc. of 0.04727 *N* HCl, 46.33, 32.02. Calcd. for $(C_2H_5)_3GeF$: F, 10.24. Found: F, 10.31, 10.53, mean, 10.42.

**Properties.**—Triethylgermanium fluoride is a colorless liquid boiling at 149.0° under a pressure of 751 mm. It has an extremely penetrating odor. The fluoride is more stable toward hydrolysis than are the other halogen derivatives.

## III. Reactions of Triethylgermanium Halides

**With Ammonia.**—The trimethyltin halides combine with one molecule of ammonia to form stable solids which are not ammonolyzed in liquid ammonia.[10] On the other hand, triethyl silicon bromide is immediately and completely ammonolyzed in the presence of ammonia, either as vapor or liquid. As was to be expected, triethylgermanium bromide exhibits intermediate properties.

**Ammino Triethylgermanium Bromide,** $(C_2H_5)_3GeBr\cdot NH_3$.—On condensing ammonia on triethylgermanium bromide, which is a solid at liquid ammonia temperature, two liquid layers are formed, the upper layer occupying the greater volume. As the ammonia evaporates, both layers gradually disappear, a white solid being left behind. The reaction tube was maintained at −33° while the uncombined ammonia was removed by means of a pump. The tube was then weighed. The increase in the weight of the tube corresponds to the weight of combined ammonia. The following results were obtained: sample, 0.7409, 3.3991; $NH_3$ combined, 0.0477, 0.2505; moles of $NH_3$ per mole $(C_2H_5)_3GeBr$, 0.906, 1.035, mean, 0.970. The results indicate that one molecule of ammonia combines with one molecule of triethylgermanium bromide. Precise results are difficult to obtain because the vapor pressure of the compound (due to ammonia) is appreciable. If the tube is pumped too long, some ammonia is lost, while if it is not pumped sufficiently, some free ammonia is left behind. Since only one molecule of ammonia is involved in the reaction, the final product was not a mixture due to ammonolysis. The compound as above prepared was analyzed for bromine.

*Anal.* Subs., 0.1769, 0.2210: AgBr, 0.1327, 0.1668. Calcd. for $(C_2H_5)_3GeBr\cdot NH_3$: Br, 31.2. Found: Br, 31.9, 32.1, mean, 32.0.

At room temperatures, the solid has a vapor pressure of 10 mm. If the vapors are removed, a liquid is left behind, which is doubtless triethylgermanium bromide. On again adding ammonia, the solid is re-formed.

The formation of two liquid layers in the presence of liquid ammonia indicates that the compound is ammonolyzed. The lower and heavier layer comprises the germanium,

[8] Starcke, *Z. anorg. Chem.*, **70,** 173 (1911).

[9] On analysis of the chlorofluoride for chlorine, it was found to be contaminated with 4% of lead chloride.

[10] Kraus and Greer, THIS JOURNAL, **45,** 3078 (1923).

as di-triethylgermaniumimine, while the upper layer contains the ammonium bromide. As the liquid ammonia is evaporated, interaction takes place between the two layers with the re-formation of the ammoniated triethylgermanium bromide.

**Reaction with Sodium in Liquid Ammonia.**—If triethylgermanium bromide is ammonolyzed in the presence of liquid ammonia as suggested above, then, on addition of an alkali metal, reaction should take place with the evolution of hydrogen. On the other hand, if no ammonolysis occurs, the bromide should be reduced to the free triethylgermanium group, which would form the dimer, hexaethyldigermane.

On adding sodium to a solution of triethylgermanium bromide in liquid ammonia a vigorous reaction occurs with evolution of hydrogen. During this reaction, the lower layer in the reaction tube remains practically unchanged.

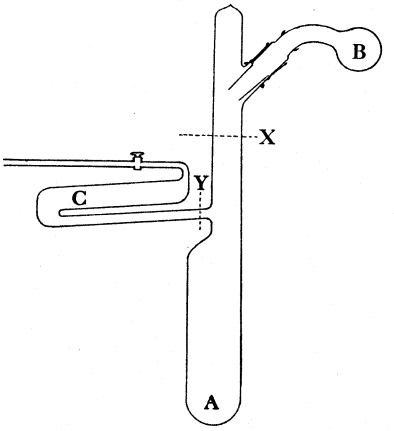


Fig. 1.—Apparatus used in preparing di-triethylgermaniumimine.

**Di-triethylgermaniumimine.**—In order to establish the nature of the lower liquid phase which contains the germanium residue after ammonolysis, a reaction was carried out in an apparatus of the form sketched in Fig. 1. Triethylgermanium bromide was introduced into the reaction chamber A, 15 cc. of liquid ammonia was condensed on the sample and sodium was added from the addition tube B. When the reaction appeared to be complete, the ammonia was allowed to evaporate and the reaction tube was sealed off at X. The tube was then turned through an angle of 90° and the high boiling liquid was distilled into C under reduced pressure. From the collecting tube C the liquid was distilled into a second tube in which the compound was filled into weighed fragile bulbs under nitrogen. These weighed samples were analyzed for germanium and nitrogen. The germanium was determined in the usual way. Nitrogen, in one analysis, was determined by the Kjeldahl method, and in another by breaking the fragile bulb, containing the sample, under ice cooled water and titrating the resulting aqueous solution with hydrochloric acid.

*Anal.* Subs., 0.1340, 0.2500: $GeO_2$, 0.0838, 0.1564. Calcd. for $[(C_2H_5)_3Ge]_2NH$: Ge, 43.41. Found: Ge, 43.40, 43.42, mean, 43.41. Subs., 0.4473, 0.4714, cc. of 0.04727 *N* HCl, 27.91, 29.25. Calcd. for $[(C_2H_5)_3Ge]_2NH$: N, 4.19. Found: N, 4.13, 4.11, mean, 4.12.

Di-triethylgermaniumimine is a colorless, mobile liquid which is insoluble in liquid ammonia. It distils at a temperature of approximately 100° under a pressure of 0.1 mm. It reacts vigorously with water to form di-triethylgermanium oxide.

**Reactions with Lithium in Ethylamine.**—Compounds of the type $R_3AX$, if they do not ammonolyze, may be reduced by means of the alkali metals in liquid ammonia with the formation of the free group which is usually obtained as a dimer. Since triethylgermanium halides are appreciably ammonolyzed in liquid ammonia, their reduction cannot be carried out in this solvent. It was thought, however, that such reduction might be effected in ethylamine, which is a weaker ammonolyzing agent. Both the bromide and the chloride react with lithium in ethylamine with the evolution of more or less hydrogen, depending upon conditions. The fluoride has less tendency to ammonolyze than do the other halides. By breaking a bulb containing the fluoride under a solution of lithium in ethylamine, reaction occurs without the evolution of hydrogen.

From the product of this reaction was obtained a high-boiling liquid which was doubtless hexaethyldigermane. Reduction takes place according to the equation

$$2(C_2H_5)_3GeX + 2Li = 2LiX + [(C_2H_5)_3Ge]_2$$

The reaction is probably complicated owing to the formation of lithium triethyl germanide. As a method for the preparation of the digermane, the reduction of the halides in ethylamine is unsatisfactory.

## IV. Hexaethyl Digermane

**Preparation.**—While triethylgermanium bromide does not react with sodium in boiling xylene, it may be conveniently reduced by the direct action of sodium on pure triethylgermanium bromide at elevated temperatures.

Twenty-five grams of triethylgermanium bromide and 10 g. of sodium were introduced into a flask which was provided with a long neck that served as an air condenser. Near the top of the condenser, the flask was connected to a mercury manometer. After introducing the reaction materials, the flask was sealed. The reaction mixture was heated on a Wood's metal bath until the sodium melted, when the metal was broken up into small droplets by shaking the tube. The temperature of the bath was then slowly raised to 210°, where the triethylgermanium bromide began to boil. The bath was maintained at this temperature for about twelve hours, during which time the pressure in the tube remained practically constant at 760 mm. The temperature of the bath was then gradually raised over a period of five days to 270°, the pressure in the manometer being raised, in the meantime, to 1200 mm. by means of a suitable leveling bulb. The pressure and temperature were always so adjusted that the level of the vapor did not rise too high in the condensing column.

At the end of the reduction process, the reaction mixture consisted of a dark blue, solid mass. The product was extracted with petroleum ether and the extract was fractionally distilled through an Eastman column.

The fraction collected between 250 and 270° was treated with strong hydrochloric acid in order to convert any ditriethyl germanium oxide to the lower boiling chloride The resulting mixture was extracted with petroleum ether, the extract was dried and fractionally distilled. The product was concentrated by repeated fractional distillations until about 10 g. of halogen-free liquid were obtained which boiled at the practically constant temperature of 265°.

*Anal.* Subs., 0.2637, 0.3385: $GeO_2$, 0.1730, 0.2215. Calcd. for $[(C_2H_5)_3Ge]_2$: Ge, 45.45. Found: Ge, 45.53, 45.42, mean, 45.47.

*Mol. wt.* (Cryoscopic method in benzene). Solvent, 12.57, 17.03; solute, 0.8798, 0.9342; $\Delta t$, 1.068, 0.857. Calcd. for $[(C_2H_5)_3Ge]_2$: 320. Found: 328, 320, mean, 324.

**Properties.**—Hexaethyldigermane is a colorless, mobile liquid of a rather pleasant odor. It boils at 265.0° under a pressure of 758 mm. and fails to solidify at −60°. It is soluble in ordinary organic solvents and in ethylamine but is insoluble in water and in liquid ammonia. Hexaethyldigermane is relatively stable toward oxygen since it may be distilled in air without noticeable change.

**Reaction of Hexaethyldigermane with Bromine.**—Hexaethyldigermane reacts readily and quantitatively with bromine to form triethylgermanium bromide. On treating the digermane with a solution of bromine in ethyl bromide, vigorous reaction occurred. On cooling to ice temperature, reaction proceeded quietly, the color disappearing almost immediately. After removing the ethyl bromide, the residual liquid was found to boil at 188° under atmospheric pressure. The boiling point of triethyl-

germanium bromide is 191°. The Ge–Ge bond is evidently broken rather readily by bromine.

**Reaction with Lithium in Ethylamine.**—Hexaethyldigermane does not react appreciably with sodium in liquid ammonia. This is in part due to the low solubility of the digermane. On adding ether to the liquid ammonia solution, appreciable reaction occurs, but it is too slow for purposes of preparation.

Lithium reacts rather readily with a solution of hexaethyldigermane in ethylamine. The reaction proceeds without the evolution of gas, which indicates that a lithium salt is formed. The solution, on completion of the reaction, has a somewhat brownish color. When the ethylamine was evaporated, on completion of the reaction, and the tube was weighed, it was found that germanium had been lost. When ammonia was condensed on the residue, after evaporation of the ethylamine, a small quantity of insoluble liquid appeared. Ammonium bromide was added to the liquid ammonia solution without noticeable effect. On evaporating the liquid ammonia and recondensing it, droplets of liquid were collected, which indicated the presence of a volatile compound carried over by the ammonia vapor.

These results indicate that lithium reacts with hexaethyldigermane to form lithium triethyl germanide according to the equation

$$[(C_2H_5)_3Ge]_2 + 2Li = 2LiGe(C_2H_5)_3$$

In ethylamine and, more completely, in ammonia, the lithium salt ammonolyzes according to the equation

$$LiGe(C_2H_5)_3 + NH_3 = (C_2H_5)_3GeH + LiNH_2$$

triethylgermane being formed.

**Triethylgermane.**—The above reaction suggests a method for the preparation of triethylgermane. A solution of 2.05 g. of hexaethyldigermane in 10 cc. of ethylamine was treated with 0.09 g. of lithium. When the reaction appeared to be complete, the ethylamine was distilled through an ice cooled trap into a suitable receiver. A small quantity of liquid (triethylgermane) condensed in the trap. The bath was removed from the trap and ammonia was passed through the trap and condensed in the reaction tube. The liquid in the trap disappeared in the course of this process. Two liquid layers were formed in the reaction tube, the lower of which was colorless and the upper of which was colored blue owing to the presence of some excess lithium. Ammonium bromide was added to the reaction mixture until the color was dispelled. Triethylgermane was present in the bottom of the reaction tube as a colorless liquid. In order to separate the volatile triethylgermane from the supernatant ammonia, the latter was withdrawn through a suitable tube which was lowered until it almost reached the surface of the liquid. The product was repeatedly washed with fresh ammonia in this way. After washing, the product was twice distilled *in vacuo*, the vapors being passed over phosphorus pentoxide in the final distillation in order to remove traces of ammonia.

The molecular weight of the final product was determined by the vapor density method, a suitable calibrated tube being used for this purpose.

*Mol. wt.* (Vap.). Subs., 0.03115, 0.03150; vol., 301.3, 301.3; pressure, mm., 12.1, 12.0; *t*, 27.0, 26.1. Calcd. for $(C_2H_5)_3GeH$: 160.7. Found: 161.1, 162.6, mean, 161.8.

*Anal.* Subs., 0.2097, 0.1923: $GeO_2$, 0.1365, 0.1250. Calcd. for $(C_2H_5)_3GeH$: Ge, 45.17. Found: Ge, 45.18, 45.12, mean, 45.15.

**Properties.**—Triethylgermane is a colorless, mobile liquid having a camphor-like odor. It boils at 124.4° under a pressure of 751 mm. It is soluble in organic solvents and insoluble in water and liquid ammonia. It readily decolorizes a solution of bromine in ethyl bromide. It does not appear to react with a solution of sodium in liquid ammonia.

It reacts readily with a solution of potassium amide in liquid ammonia with the evolution of a gas, presumably hydrogen. Potassium triethyl germanide, therefore, cannot be prepared by the action of potassium amide on triethylgermane.

**Reaction of Hexaethyldigermane with Potassium in Ethylamine.**—The preceding experiments indicate that lithium triethyl germanide is largely ammonolyzed in ethylamine and completely so in ammonia. Since potassium amide is a much stronger base than lithium amide, it was thought that potassium triethyl germanide might be stable in liquid ammonia solution.

The salt was prepared by the direct action of metallic potassium on a solution of hexaethyldigermane in ethylamine. 0.37 g. of the digermane was introduced into leg B of the reaction tube shown in Fig. 2 and 0.089 g. of potassium was introduced into leg A. Liquid ammonia was condensed upon the metal and the solution was evaporated rapidly so as to distribute the potassium as a thin film over the inner wall of leg A, thus exposing a large surface. After exhausting the tube, ethylamine was condensed in leg A. Tubes F and E were then sealed and ethylamine was decanted into leg B and returned to leg A, the process being repeated until all the digermane had been washed into leg A. The tube was then left for a period of six weeks, at the end of which time the metal had disappeared completely and a clear yellow solution was present in leg A. The reaction tube was now attached to the system and the stopcock D was turned, breaking the end of the capillary H. The ethylamine was distilled from the solution in A and, after exhausting thoroughly, ammonia was condensed on the solid material that remained behind. There was no evidence of ammonolysis, a clear yellow solution being formed. Presumably, this was a solution of potassium triethyl germanide in liquid ammonia.

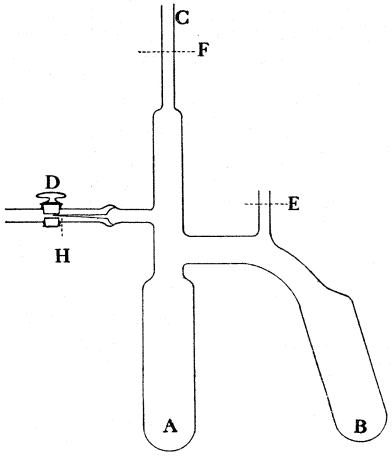

Fig. 2.—Apparatus for preparing potassium triethyl germanide.

To definitely establish this fact, the tube F was cut and ethyl bromide was added until the color of the solution in A was completely discharged. As the reaction proceeded, an insoluble liquid separated from solution and settled to the bottom. The ammonia was now evaporated, the residual liquid extracted with petroleum ether and, after drying, the petroleum ether was removed by distillation. The remaining liquid was distilled and collected in two fractions. Nearly all the liquid was collected in the first fraction, which boiled at 162–164°, identifying it as germanium tetraethyl (b. p. 163.8°). The other fraction had a very high boiling point, and probably was hexaethyldigermane, a slight excess of which was used in the original preparation.

Potassium triethylgermanide was evidently formed in ethylamine according to the equation

$$[(C_2H_5)_3Ge]_2 + 2K = 2KGe(C_2H_5)_3$$

On addition of ethyl bromide to the ammonia solution of the potassium salt, reaction took place as follows

$$C_2H_5Br + KGe(C_2H_5)_3 = Ge(C_2H_5)_4 + KBr$$

Potassium triethyl germanide may evidently be prepared as above described in practically quantitative yield.

## Summary

A convenient method is described for the preparation of tetraethylgermane which gives excellent yields.

The preparation of the triethylgermanium halides and of di-triethylgermanium oxide is described and some of their more common properties are recorded.

The reaction of the triethylgermanium halides with ammonia and with solutions of the alkali metals in ammonia and ethylamine have been studied. The preparation of di-triethylgermanylimine is described.

The preparation of hexaethyldigermane is described. The reaction of this digermane with the alkali metals in ammonia and ethylamine has been studied. The preparation of triethylgermane is described as are also some of its reactions.

A method is described for the preparation of potassium triethylgermanide.


PROVIDENCE, RHODE ISLAND

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE FRIEDRICH WILHELM UNIVERSITY IN BERLIN]

# THE REACTION BETWEEN KETOXIDO COMPOUNDS AND GRIGNARD REAGENTS

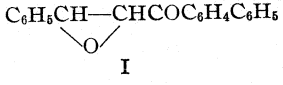
BY ERNST BERGMANN AND H. A. WOLFF

RECEIVED NOVEMBER 30, 1931 PUBLISHED APRIL 6, 1932

In a recent communication[1] Kohler and co-workers describe experiments on the reaction of ketoxido compounds with Grignard reagents. Benzalacetophenone oxide, for instance, is transformed into triphenylcarbinol by phenylmagnesium bromide

$$C_6H_5CH\text{—}CHCOC_6H_5 \longrightarrow (C_6H_5)_3COH$$
$$\quad\quad\quad

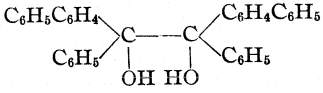
mary reaction phenyl biphenyl ketone (III) is formed, which is reduced to the pinacol by the action of the finely divided magnesium resulting from the preparation of the Grignard reagent. The structure of the compound is demonstrated not only by the analytical results but also by the deep green color reaction of sodium ethoxide on its benzene solution (formation of the ketyl).[2]



I

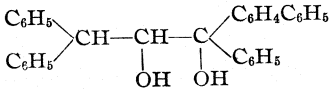


III

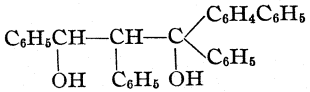


II

The second product is a well-defined compound, $C_{33}H_{28}O_2$, resulting from the addition of two moles of phenylmagnesium bromide to compound (I), doubtless to the carbonyl group *and* to the ethylene oxide ring. The two possible formulas for the second compound are IV or V, the latter being more probable in view of those reactions of ethylene oxide with Grignard reagents already known.[3]

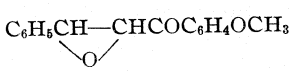


IV

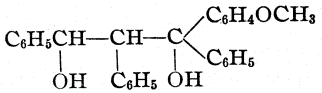


V

The reaction between phenylmagnesium bromide and benzal-*p*-methoxyacetophenone oxide (VI) leads also, by the addition of two moles of the reagent, to a compound, $C_{28}H_{26}O_3$, to which we assign formula VII. Experiments leading to the synthesis of this compound have not been successful as yet.



VI



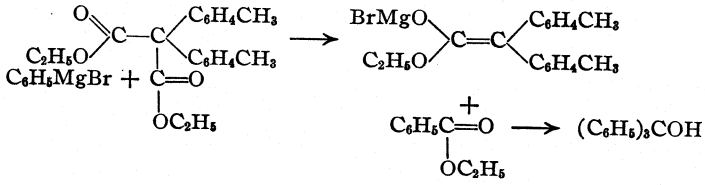
VII

Compounds I and II were synthesized in the usual way. Cinnamoyl chloride was condensed with anisole or diphenyl by means of aluminum chloride and the unsaturated ketone was oxidized by alkaline hydrogen peroxide. From (I) we have isolated the two possible stereoisomers (*cis* and *trans*) but the experiments were carried out only with the lower melting main product. We believe that such a pair of isomeric ketoxido compounds has not yet been described in the literature.

[2] Whether the pinacol (m. p. 181°) is the same as that described by Gomberg and Bachmann [THIS JOURNAL, **49**, 236 (1927); m. p. 198–199°] or its diastereoisomer we are unable to decide, since the melting points of pinacols which undergo disproportionation on heating are by no means characteristic constants [*cf.* Bergmann and Fujise, *Ann.*, **480**, 65–74 (1930)].

[3] *Cf.* Houben-Weyl, "Die Methoden der organischen Chemie," Vol. IV, p. 781.

In our laboratory we have observed in many cases the scission of relatively highly phenylated compounds by means of Grignard reagents. For example,[4] ethyl di-*p*-tolylmalonate and an excess of phenylmagnesium bromide produce triphenylcarbinol and ethyl di-*p*-tolylacetate. Doubtless, in the first step, ethyl benzoate and the enolate of ethyl di-*p*-tolylacetate are formed. The latter cannot react with the Grignard compound, so the former is converted into triphenylcarbinol



In this connection it is of interest that Boeseken and Kremer[5] recently have observed that benzalacetone, in a closely analogous manner, is transformed by means of peracetic acid into styryl acetate

$$C_6H_5CH{=}CHCOCH_3 \longrightarrow C_6H_5CH{=}CHOCOCH_3$$

## Experimental Part

**Cinnamoyl chloride** was prepared by boiling 120 g. of cinnamic acid with 250 g. of thionyl chloride for two hours. The excess of thionyl chloride was evaporated on the steam-bath and the residue was distilled *in vacuo*, b. p. 130° (14 mm.). The yield was 120 g.

**Benzal-*p*-methoxyacetophenone** was prepared according to the procedure of Stockhausen and Gattermann,[6] by condensing 44 g. of anisole and 67 g. of cinnamoyl chloride in 100 cc. of carbon disulfide by means of 50 g. of finely powdered aluminum chloride. The reaction is a vigorous one and was completed by four hours of boiling on the water-bath. The mass was decomposed by means of ice and fuming hydrochloric acid, the solution dried and distilled. The ketone boils at 265° (21 mm.) and crystallizes rapidly, m. p. 107°. The yield is very good.

**Benzal-*p*-methoxyacetophenone Oxide (VI).**—A solution of 12 g. of the unsaturated ketone in 150 cc. of hot methanol was rapidly cooled and the crystalline powder formed was shaken with 10 cc. of a 20% solution of potassium hydroxide and 15 cc. of a 15% solution of hydrogen peroxide. After half an hour the mixture was poured into water and the precipitate recrystallized from methanol as colorless crystals, m. p. 75°.

*Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.5. Found: C, 75.3; H, 5.5.

**1,2,3-Triphenyl-3-*p*-anisyl-1,3-dihydroxypropane (VII).**—Five grams of the oxide VI was added to a Grignard solution prepared from 10.5 cc. of bromobenzene and 2 g. of magnesium turnings. After decomposing with ice and dilute sulfuric acid and evaporating the ether, the glycol was recrystallized from benzene or ethyl acetate as needles of m. p. 131–132°. The yield was 3 g.

*Anal.* Calcd. for $C_{28}H_{26}O_3$: C, 82.0; H, 6.3; $OCH_3$, 7.5; mol. wt., 410. Found: C, 82.2; H, 6.5; $OCH_3$, 7.2; mol. wt., 390, 397.

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[4] *Cf.* H. Mirau, Thesis, Berlin, 1927.

[5] Boeseken and Kremer, *Rec. trav. chim.*, **50**, 827 (1931).

[6] Stockhausen and Gattermann, *Ber.*, **25**, 3336 (1892).

**Benzal-*p*-phenylacetophenone.**—To a solution of 60 g. of diphenyl and 60 g. of cinnamoyl chloride in 300 cc. of carbon disulfide, 50 g. of aluminum chloride was added in small portions during fifteen minutes. The reaction product was boiled for two hours, decomposed with ice and fuming hydrochloric acid and worked up in the usual manner. The ketone crystallized from propanol in small prisms, m. p. 165°. The yield was 70 g.

*Anal.* Calcd. for $C_{21}H_{16}O$: C, 88.7; H, 5.6. Found: C, 88.5; H, 6.0.

**Benzal-*p*-phenylacetophenone Oxide. (I).**—To a well-stirred solution of 20 g. of benzal-*p*-phenylacetophenone in 100 cc. of 1,4-dioxane 20 cc. of a 25% solution of potassium hydroxide and 25 cc. of a 15% solution of hydrogen peroxide were added. After half an hour the mixture was poured into water, filtered and dried. The lower melting isomer is soluble in boiling alcohol and crystallizes on cooling; yield, 15 g.; m. p. 126°.

*Anal.* Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3. Found: C, 84.5; H, 5.4.

The other isomer, which is insoluble in alcohol, was recrystallized from glacial acetic acid. The yield was 1.5 g. of m. p. 162°.

*Anal.* Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3; mol. wt., 300. Found: C, 84.4; H, 5.4; mol. wt., 293.

Both the isomers oxidize potassium iodide in acetic acid solution, a reaction typical of ketoxido compounds.[7]

**Benzal-*p*-phenylacetophenone Oxide (I) and Phenylmagnesium Bromide.**—Ten grams of oxide I was added to a Grignard solution prepared from 20 cc. of bromobenzene and 5 g. of magnesium. The reaction product was worked up in the usual manner and gave a thick oil from which, on digestion with glacial acetic acid, crystals were deposited. It crystallized from xylene in prisms of m. p. 181° which were identified as a pinacol (II) of phenyl biphenyl ketone by analysis and by its color reaction on addition of sodium ethoxide.

*Anal.* Calcd. for $C_{38}H_{30}O_2$: C, 88.0; H, 5.8. Found: C, 87.9; H, 5.9.

From the mother liquors, on standing, an oil was obtained which crystallized gradually. The crystals gave a violet color reaction with concentrated sulfuric acid. The substance was recrystallized from xylene, m. p. 159°. The compound is 1,1,3-triphenyl-3-biphenylyl-1,3-dihydroxypropane (V).

*Anal.* Calcd. for $C_{33}H_{28}O_2$: C, 86.8; H, 6.1; mol. wt., 456. Found: C, 87.1; H, 6.2; mol. wt., 456.

## Summary

According to Kohler and his co-workers, ketoxido compounds such as benzalacetophenone oxide are cleaved by means of aromatic Grignard reagents. In the first step the aroyl group is converted into a diaryl ketone.

From benzal-*p*-phenylacetophenone oxide and phenylmagnesium bromide two products are formed, a pinacol of phenyl biphenyl ketone, this being formed in the first reaction, and the "normal reaction product," 1,1,3-triphenyl-3-biphenylyl-1,3-dihydroxypropane.

From benzal-*p*-methoxyacetophenone oxide and phenylmagnesium bromide 1,1,3-triphenyl-3-*p*-anisyl-1,3-dihydroxypropane is obtained as the sole product.

BERLIN, GERMANY

[7] *Cf.* Bergmann and Hervey, *Ber.*, **62**, 896 (1929).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# HEXYL AND HEXENYL DERIVATIVES OF PHENOL

BY CHARLES D. HURD AND R. W. MCNAMEE

RECEIVED NOVEMBER 30, 1931 PUBLISHED APRIL 6, 1932

Phenoxy-1-hexene-2 or γ-*n*-propylallyl phenyl ether, $C_6H_5—O—CH_2-CH=CH—C_3H_7$, was prepared and studied. The bromo-1-hexene-2, from which it was synthesized, was made by the action of hydrobromic acid on hexene-1-ol-3

$$CH_2=CH—CHOH—C_3H_7 \xrightarrow[H_2SO_4]{HBr} BrCH_2CH=CHC_3H_7$$

Chloro-1-hexene-2 was also prepared and its structure established both by hydrogenation into *n*-hexyl chloride and by hydrolysis to hexene-2-ol-1.

Hydrogenation of phenoxy-1-hexene-2 gave rise to phenyl *n*-hexyl ether. The latter was also prepared from sodium phenoxide and *n*-hexyl chloride.[1] The ether was crystallized for the first time. When phenoxy-1-hexene-2 was pyrolyzed, rearrangement into a phenol, *o*-hydroxyphenyl-3-hexene-1, occurred.

$$C_6H_5—O—CH_2CH=CHC_3H_7 \longrightarrow C_6H_4\begin{cases}OH\\CH(C_3H_7)—CH=CH_2\end{cases}$$

For purposes of comparison, 3-phenoxyhexane and *o*-hydroxyphenyl-1-hexene-2 were synthesized.

**Chloro-1-hexene-2.**—This synthesis and also its proof of structure by hydrogenation were performed by Dr. Frank L. Cohen. Fourteen grams of hexene-1-ol-3,[2] b. p. 52–53° (20 mm.) and $n_D^{16}$ 1.4269, was dissolved in 20 cc. of benzene and 7 g. of phosphorus trichloride was added to it dropwise. The next day the benzene layer was decanted, washed with cold water, dried over calcium chloride and distilled. The chlorohexene was collected at 35–50° and 40 mm. Redistillation at atmospheric pressure gave these fractions: 3 g., 110–118°, $n_D^5$ 1.4630; 6 g., 120–123°, $n_D^5$ 1.4565; 6 g., 123–129°, $n_D^5$ 1.4520. In another run, 40 g. of the hexene-1-ol-3 was used and 34 g. of the chlorohexene was formed. A portion boiling at 42–44° (40 mm.) or 120–122° (751 mm.) was analyzed.

*Anal.* Calcd. for $C_6H_{11}Cl$: Cl, 29.46. Found: Cl, 30.1, 29.57.

**Proof of Structure.**—The chlorohexene was reduced by hydrogen, using Adams' platinum oxide catalyst. A saturated chloride was obtained, b. p. 126–127°, which was then hydrolyzed into the corresponding alcohol by refluxing with a 10% solution of sodium hydroxide. The alcohol thus obtained was converted into the dinitrobenzoate ester, m. p. 53–54°. A mixed melting point determination with known *n*-hexyl dinitrobenzoate was 53–55°. Since hydrogenation of unsaturated compounds proceeds without rearrangement, it is established that the compound studied was chloro-1-hexene-2, and not chloro-3-hexene-1.

**Bromo-1-hexene-2.**—Twenty grams of hexene-1-ol-3 was added to a mixture of

[1] Tronov and Ladigina, *Ber.*, **62**, 2844 (1929) used hexyl bromide; Dionneau, *Ann. chim.*, [9] **3**, 209 (1915), used magnesium on 5-iodo-1-phenoxyhexane.

[2] Delaby, *ibid.*, [9] **19**, 287 (1923); Bouis, *ibid.*, [10] **9**, 409 (1928).

48 g. of hydrobromic acid (48%) and 13 g. of sulfuric acid. The mixture was left overnight, then was ether-extracted, the ether solution washed with cold water, dried and distilled: yield, 23 g.; b. p. 43–45° (10 mm.), 50–53° (25 mm.); $n_D^{16}$ 1.4770. Bouis[3] prepared this halide using phosphorus tribromide and pyridine, rather than hydrobromic and sulfuric acids.

**Hydrolysis of the Halides.**—Ten grams of sodium hydroxide in 25 cc. of water was refluxed for two and one-half hours with 4.5 g. of bromo-1-hexene-2. The mixture was ether-extracted, the extract dried over calcium chloride and distilled *in vacuo*. Three cc. of hexene-2-ol-1 was collected at 54–57° (20 mm.); $n_D^{25}$ 1.4490. Similarly, 4 g. of chloro-1-hexene-2 was hydrolyzed into 2 cc. of the same alcohol; $n_D^{25}$ 1.4485. The refractive index is considerably higher than the index for hexene-1-ol-3.

### γ-*n*-Propylallyl Phenyl Ether (Phenoxy-1-hexene-2)

**(a) From Bromo-1-hexene-2 (or Chloro-1-hexene-2) and Sodium Phenoxide in Alcohol.**—Three grams of sodium was dissolved in 75 cc. of absolute alcohol, after which 9.5 g. of phenol was added. To the sodium phenoxide solution thus prepared, 16 g. of bromo- (or chloro-)-1-hexene-2 was added. Cooling under the tap was necessary to control the reaction. The mixture was left overnight, after which 120 cc. of water was added. It was ether extracted, the extract washed with dilute alkali and then with water, dried and distilled. Eleven grams of a fraction, b. p. 125–128° (12 mm.), was obtained. Mr. M. P. Puterbaugh has confirmed these directions.

*Anal.* Calcd. for $C_{12}H_{16}O$: C, 81.75; H, 9.15. Found: C, 81.8; H, 9.0.

**(b) From Bromo-1-hexene-2, Phenol and Potassium Carbonate.**—Sixteen grams of the bromide was added to a solution of 9.5 g. of phenol in 75 cc. of dry ether. Into it was added 15 g. of dry potassium carbonate and 30 cc. of dry acetone. The mixture was refluxed for two hours. It was left overnight and worked up as before; yield, 14 cc. Mr. Puterbaugh also tested this method and obtained a 25.5 g. (57%) yield, using 41 g. of the bromide, 23.5 g. of phenol, 34.5 g. of potassium carbonate and 50 cc. of acetone (no ether). These constants characterized the phenoxy-1-hexene-2: b. p. 105–107° at 4–5 mm., $d_4^{20}$ 0.9408, $n_D^{15}$ 1.5130, $n_D^{20}$ 1.5109. The corresponding reaction between chloro-1-hexene-2, phenol and potassium carbonate (or pyridine) failed. Most of the chloride was recovered after five hours of refluxing.

**Ortho γ-*n*-Propylallylphenol (*o*-Hydroxyphenyl-1-hexene-2).**—Five grams of phenol was dissolved in 100 cc. of dry ether[4] at 5° and 1.5 g. of sodium ribbon was inserted. After the first violent reaction, the mixture was heated till the sodium was consumed. Then 5 g. of chloro-1-hexene-2 was added, the mixture refluxed for six hours, filtered, and 50 cc. of ether added. It was washed with water, dried, the ether evaporated and the residue distilled at 20 mm. After collecting a small amount of phenol at 80°, the temperature rose rapidly to 144°. A viscous, colorless liquid (3–4 cc.) was obtained; $n_D^{25}$ 1.5250. This *o*-propylallylphenol was insoluble in sodium bicarbonate solution but soluble in 5% potassium hydroxide solution.

*Anal.* (Zerewitinoff). Calcd. for $C_6H_{11}C_6H_4OH$: OH, 1.00. Found: OH, 0.98.

### New Syntheses of Phenyl *n*-Hexyl Ether (1-Phenoxyhexane)

**(a) From Phenoxy-1-hexene-2.**—Three cc. of the compound was hydrogenated catalytically using 0.2 g. of the Adams' platinum oxide catalyst, 25 cc. of alcohol and

[3] Bouis, *Ann. chim.*, [10] 9, 421 (1928).

[4] Similar C-alkylations, using ether instead of alcohol, which promotes O-alkylation, have been studied by Claisen, *Z. angew. Chem.*, **36**, 478 (1923); Claisen and others, *Ann.*, **442**, 210 (1925).

hydrogen. Reduction was rapid and reaction ceased when the calculated quantity of hydrogen had been absorbed. After filtration and distillation (b. p. 126–130° (12 mm.)) of the filtrate, 2.5 cc. of phenyl hexyl ether was collected.

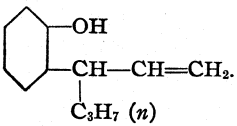
**(b) From *n*-Hexyl Chloride (Williamson Synthesis).**—Hexyl alcohol was synthesized from *n*-butylmagnesium bromide and ethylene oxide. After conversion to hexyl chloride, 8 g. of it was added to a solution of sodium phenoxide (2 g. of sodium, 6.5 g. of phenol) in absolute alcohol (75 cc.). The mixture was left for a day and then refluxed for two hours. Some alcohol was evaporated off, then water was added and the mixture ether extracted, the extract washed with dilute alkali, dried and distilled. Three cc. of phenyl hexyl ether was obtained, b. p. 125–128° at 11 mm.

**Physical Properties.**—Following a redistillation, the phenyl hexyl ether from either (a) or (b) gave these constants: $n_D^{25}$ 1.4889, $d_4^{25}$ 0.918. By strong cooling, it solidified readily to fine, hard crystals; m. p. −19°.

**3-Phenoxyhexane, $C_6H_5$—O—$CH(C_2H_5)$—$CH_2CH_2CH_3$.**—3-Hexanol, prepared from *n*-butyraldehyde and ethylmagnesium bromide, was converted into 3-bromohexane by the action of 48% hydrobromic acid and sulfuric acid. Ten grams of the bromide was heated for four hours in absolute alcohol (60 cc.) with sodium phenoxide (6 g. of phenol, 2 g. of sodium). The details were similar to the Williamson synthesis of 1-phenoxyhexane. Four cc. of the ether was obtained: b. p. 129–132° (12 mm.); $d_4^{25}$ 0.923; $n_D^{25}$ 1.4893. The melting point of −35 to −33.5° was obtained on crystals obtained by cooling the liquid to −78°. The bulb of a corrected toluene thermometer was immersed in the melting crystals.

*Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.1. Found: C, 81.0, 80.97; H, 9.90, 9.98.

**Pyrolysis of γ-*n*-Propylallyl Phenyl Ether.**—Three cc. of the ether was placed in a side-arm test-tube which was heated uniformly by a bath. Rearrangement,[5] as evidenced by an exothermic reaction, occurred at 210–215°. When the temperature of the liquid reached 292°, 1.5 cc. of liquid distilled which, after redistillation at 12 mm., gave $n_D^{25}$ 1.5244. The phenol dissolved in dilute alkali and analysis confirmed the presence of one hydroxyl. Presumably it was *o*-hydroxyphenyl-3-hexene-1.




*Anal.* (Zerewitinoff). Calcd. for $C_{12}H_{15}OH$: OH, 1.00. Found: OH, 0.97.

In duplicating this pyrolysis with a 20-g. sample of the ether, Mr. M. P. Puterbaugh identified ordinary phenol as well as the higher phenol. The 2 g. of phenol was collected at 80–85° at 6–7 mm. and it solidified in the receiver. There was 2 g. of an intermediate fraction (b. p. 85–120°), following which 8 g. (a 40% yield) of hydroxyphenyl-3-hexene-1 distilled at 120–122° (7 mm.). Index of refraction data on this fraction were $n_D^{15}$ 1.5275, $n_D^{20}$ 1.5255. Zerewitinoff analysis for hydroxyl gave a value of 0.98. About 4 g. of a fourth fraction was collected at 7 mm. between 135–165°.

## Summary

Chloro-1-hexene-2 and bromo-1-hexene-2 were synthesized and their structures established by hydrolysis into hexene-2-ol-1. Hydrogenation of the chloride yielded *n*-hexyl chloride. Phenoxy-1-hexene-2, on reduction, yielded phenyl *n*-hexyl ether. The latter was also made by the Williamson reaction, as was 3-phenoxyhexane. Above 215°, phenoxy-1-hexene-2 rearranged into *o*-hydroxyphenyl-3-hexene-1, a phenol resembling the isomeric

[5] Compare Hurd and Cohen, THIS JOURNAL, 53, 1917 (1931).

*o*-hydroxyphenyl-1-hexene-2, which was synthesized for purposes of comparison. The physical properties of these compounds were determined.

EVANSTON, ILLINOIS

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# THE USE OF NICKEL AS A CATALYST FOR HYDROGENATION. II

BY LLOYD W. COVERT, RALPH CONNOR AND HOMER ADKINS

RECEIVED DECEMBER 2, 1931 PUBLISHED APRIL 6, 1932

A study of the preparation of nickel catalysts[1] indicated that in general sodium bicarbonate was to be preferred to sodium carbonate or potassium hydroxide as a precipitant in the preparation of nickel catalysts. This was true because the resulting catalysts were somewhat more active and less sensitive to variations in the procedure of preparation. More recently it has become evident that ammonium carbonate is in general the most satisfactory precipitant.

**Procedure Recommended for the Preparation of a Nickel Catalyst.**—Fifty-eight grams of Baker and Adamson or Mallinckrodt C. P. nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), dissolved in 80 ml. of distilled water, was ground for thirty to sixty minutes in a mortar with 50 g. of acid washed kieselguhr (*ex* Johns-Manville "Filter-Cel") until the mixture was apparently homogeneous and flowed as freely as a heavy lubricating oil. It was then slowly added to a solution prepared from 34 g. of Mallinckrodt C. P. ammonium carbonate, monohydrate ($(NH_4)_2CO_3 \cdot H_2O$)) and 200 ml. of distilled water. The resulting mixture was filtered with suction, washed with 100 ml. of water in two portions, and dried overnight at 110°. The yield was 66 g. Just before use, 2 to 6 g. of the product so obtained was reduced for one hour at 450° in a stream of hydrogen which passed over the catalyst at a rate of 10 to 15 ml. per minute. The catalyst was then cooled to room temperature and transferred in a stream of hydrogen to the reaction vessel, which had been filled with carbon dioxide.

**Time of Reduction, Nickel Content and Activity of Catalysts.**—Some years ago the time and temperature for the reduction of nickel on a kieselguhr support in this Laboratory was rather arbitrarily set as one hour at 450°, since this gave a catalyst of good activity. Diwoky in this Laboratory observed that for certain rather inactive preparations the catalyst was more active if a higher temperature or a longer time was used in the reduction of the nickel oxide. On the basis of this observation it seemed desirable to ascertain the optimum conditions for the reduction of various types of nickel catalysts. Armstrong and Hilditch[2] showed that the activity of

[1] Adkins and Covert, *J. Phys. Chem.*, **35**, 1684–1691 (1931).

[2] Armstrong and Hilditch, *Proc. Roy. Soc.* (London), **99A**, 490–495 (1921).

nickel catalysts increased with the content of metallic nickel, so that analyses for nickel in combination with other elements were made upon the catalyst before reduction and analyses for metallic nickel after reduction. There is recorded in Table I a summary of significant data on the relationship of temperature and time of reduction, content of nickel and catalytic activity as measured against acetone.

TABLE I

EFFECT OF TIME AND TEMPERATURE UPON EXTENT OF REDUCTION AND ACTIVITY OF NICKEL ON KIESELGUHR

| Catalyst | Reduction Temp., °C. | Reduction Time, minutes | Metallic nickel, %[b] | Time for reduction of acetone[c] "Middle 60%" | Time for reduction of acetone[c] 100% |
|---|---|---|---|---|---|
| No. 8. Kieselguhr nickel nitrate added to soln. of $Na_2CO_3$ (12.6% Ni) | 450 | 30 | .. | 26 | 52 |
| | 525 | 30 | .. | 22 | 55 |
| | 525 | 45 | .. | 17 | 35 |
| | 450 | 60 | 5.14 | 23 | 39 |
| | 500 | 60[a] | 7.66 | 10 | 16 |
| | 550 | 60 | .. | 16 | 26 |
| | 450 | 90 | .. | 17 | 25 |
| No. 15. Soln. of $Na_2CO_3$ added to kieselguhr nickel nitrate (12.5% Ni) | 450 | 30 | .. | 20 | 40 |
| | 525 | 30 | .. | 21 | 59 |
| | 525 | 45 | .. | 17 | 35 |
| | 450 | 60 | 5.14 | 21 | 47 |
| | 500 | 60[a] | 7.38 | 18 | 30 |
| | 550 | 60 | .. | 21 | 85 |
| | 450 | 90 | .. | 29 | 40 |
| No. 16. Soln. of $NaHCO_3$ added to kieselguhr nickel nitrate (13.6% Ni) | 450 | 30 | .. | 86 | 150 |
| | 525 | 30 | .. | 24 | 45 |
| | 525 | 45 | .. | 44 | 74 |
| | 450 | 60 | 9.88 | 11 | 30 |
| | 500 | 60[a] | 10.2 | 21 | 60 |
| | 550 | 60 | .. | 103 | 160 |
| | 450 | 90 | .. | 10 | 25 |
| No. 24. Kieselguhr nickel nitrate added to soln. of $(NH_4)_2CO_3$ (14.9% Ni) | 450 | 60 | 10.4 | 10 | 23 |
| | 500 | 60 | 10.3 | 25 | 55 |
| No. 23. Soln. of $(NH_4)_2CO_3$ added to kieselguhr nickel nitrate (13.6% Ni) | 450 | 60 | 7.85 | 10 | 20 |
| | 500 | 60 | 7.95 | 19 | 45 |

[a] The content of metallic nickel was not materially increased by longer times for reduction even up to five hours.

[b] Metallic nickel was determined by a standard method (Treadwell and Hall, "Quantitative Analysis," John Wiley and Sons, New York City, Vol. II, 1928, p. 520) except that ferric sulfate was substituted for ferric chloride. The dimethylglyoxime method was used for the determination of total nickel.

[c] 1.0 mole of acetone, 2 g. of catalyst, 125°, 125 atmospheres pressure.

In brief it may be said that for one of the sodium carbonate catalysts (8), sixty minutes at 500° were the optimum conditions, while ninety

minutes at 450° or sixty minutes at 550° gave identical and inferior catalysts. For the bicarbonate catalyst (16), sixty to ninety minutes at 450° were the best conditions, while a shorter time at 450° or a higher temperature are definitely deleterious in their effect upon the activity of the catalyst. For catalyst 15 (sodium carbonate type B), the relative merits of the different conditions for the reduction of the catalyst were dependent upon whether the basis of comparison for activity is the time for the "middle 60%" reduction of acetone or the time for complete reduction. On the former basis quite similar activity was found for five sets of conditions for the reduction of the catalyst. On the basis of a comparison of the time required for the complete hydrogenation of acetone, temperatures above 500° and times over sixty minutes are definitely injurious. There appears to be no reason why longer than sixty minutes or temperatures higher than 450° should be used for the reduction of the ammonium carbonate type of catalysts (23 and 24).

A correlation of the data on the content of metallic nickel with the activity of the catalysts makes it clear why higher temperatures and longer times were required for the reduction of the sodium carbonate (8 and 15) than for the bicarbonate (16) or ammonium carbonate catalysts (23 and 24) and in part why the latter were more active. Although it is evident that the activity was not strictly proportional to the content of reduced nickel, yet it is significant that the sodium carbonate catalysts had a less content of nickel originally, and the nickel compound was reduced to metallic nickel more slowly at 450° than was true for the bicarbonate or ammonium carbonate catalysts. Moreover, for all the catalysts there was a considerable proportion of the nickel which was not reduced even after several hours, but this proportion was greater for the sodium carbonate catalysts. The deleterious effect of longer times and higher temperatures than the optimum is, of course, due to the well-known slow deactivation of metallic catalysts at temperatures above perhaps 400°.

**Promotion of Nickel Catalysts for Hydrogenation.**—There are numerous claims in the literature, especially in patents, with regard to the promotion of the activity of nickel catalysts through the inclusion of another element. A group of catalysts was therefore made up by the bicarbonate method which contained in addition to nickel either copper, zinc, chromium, molybdenum, barium, manganese, cerium, iron, cobalt, boron, silver, magnesium, tungsten, tin or silicon (other than in the kieselguhr). These catalysts were tested in the hydrogenation of acetone, the diethyl acetal of furfural, and to a limited extent on toluene. A summary of the data is given in Table II. The activity of the catalyst may be compared on the basis; (1) of the observed "inflection temperature," *i. e.*, the temperature at which the pressure in the bomb reached its maximum,

or (2) on the basis of the percentage of the compound reduced below 125° for acetone and 175° for the acetal, or (3) on the basis of the time required for complete hydrogenation. The first two of these bases give an indication of the initial activity of the catalyst at lower temperatures, while the third is the most significant from a practical standpoint.

In the case of acetone, activity was promoted by molybdenum, tin, chromium, cobalt and boron, while tungsten reduced the activity of the

TABLE II

EFFECT OF VARIOUS ELEMENTS UPON THE CATALYSIS BY NICKEL OF THE HYDROGENATION OF ACETONE[a] AND THE ETHYL ACETAL OF FURFURAL[b]

| Catalysts[c] | Inflection temp. Acetone | Inflection temp. Acetal | % Hydrogenated Below 125° Acetone | % Hydrogenated Below 175° Acetal | Minutes for 100 % hydrogenation Acetone | Minutes for 100 % hydrogenation Acetal[h] |
|---|---|---|---|---|---|---|
| Ni | 100 | 118 | 18 | 83 | 13 | 12 |
| +Cu | 105 | 108 | 30 | 85 | 25 | 10 |
| +Cu[d] | 105 | 120 | 28 | 88 | 16 | 12 |
| +Zn | 125 | 110 | 16 | 40 | 15 | 160[e] |
| +Cr | 95 | 105 | 38 | 96 | 16 | 11 |
| +Mo | 80 | 105 | 47 | 100 | 10 | 0 |
| +Ba | 100 | 100 | 33 | 96 | 24 | 1 |
| +Mn | 100 | 138 | 20 | 100 | 24 | 0 |
| +Ce | 100 | 115 | 28 | 100 | 20 | 0[g] |
| +Fe | 112 | 130 | 17 | 100 | 16 | 0[g] |
| +Co | 100 | 125 | 35 | 88 | 10 | 8[g] |
| +B | 100 | 108 | 30 | 88 | 10 | 16[g] |
| +Ag | 100 | 105 | 24 | 63 | 15 | 11[g] |
| +Mg | 95 | 108 | 27 | 98 | 12 | 8 |
| +W | 120 | 130 | 12 | 92 | 140 | 17[g] |
| +Sn | 80 | 105 | 46 | 63 | 16 | 71[g] |
| +Si | 100 | 110 | 28 | 100 | 16 | 0[g] |
| +Ce | 115[f] | | 40[f] | | 4[f] | |
| +Cu | 115[f] | | 24[f] | | 15[f] | |
| +Ba | 110[f] | | 30[f] | | 24[f] | |

[a] 1.0 mole of acetone, 2 g. of catalyst, 125° and 125 atm. pressure.

[b] 0.25 mole of acetal, 2 g. of catalyst, 175° and 125 atm. pressure.

[c] Unless otherwise noted catalysts referred to in this table were prepared by the addition of a solution of sodium bicarbonate to nickel nitrate on kieselguhr. One part of copper, zinc, chromium, barium or manganese as nitrates was incorporated into the kieselguhr along with ten parts of nickel nitrate. One part of molybdenum as ammonium molybdate, boron as borax, tungsten as sodium tungstate, or silicon as sodium silicate was added to the nickel nitrate (10 parts) kieselguhr mixture just before the addition of the precipitant.

[d] The precipitant was sodium carbonate.

[e] Two applications of catalyst were necessary.

[f] These figures are for the hydrogenation of toluene at 175°.

[g] The rate of hydrogenation was so rapid as to make it necessary to stop the rocking of the bomb in order to avoid an excessive rise in temperature.

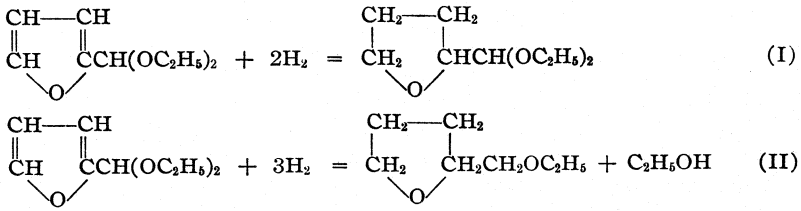
[h] The yield of saturated acetal in only one of these hydrogenations was more than a few per cent., and in most of them it was zero. The bicarbonate catalyst containing copper gave a 30% yield of the saturated acetal.

nickel. Against the acetal, molybdenum, barium, manganese, cerium, iron and silicon exerted a promoting effect, while zinc was as deleterious in this hydrogenation as was tungsten for acetone. Cerium distinctly promoted the hydrogenation of toluene.

It is apparent that these so-called promoters are so specific in their action that an element that promotes the hydrogenation of one compound may inhibit that of another. It is further apparent that none of the promoters tested greatly increased the activity of the nickel catalyst.

**Competitive Hydrogenations.**—The most interesting hydrogenations are those in which there are simultaneous reactions resulting in two or more products both of which are resistant to further hydrogenation under the given conditions. It was previously shown[1] that the ratio of cyclohexylcarbinol to toluene produced by the hydrogenation of benzyl alcohol varied from 1 : 2 to 1 : 9, and the ratio of cyclohexanediol to cyclohexanol produced from resorcinol varied from a ratio of 9 : 1 to 1 : 3, with changes in the method of preparation of the nickel catalyst.

Previous investigators have found that the hydrogenation of acetals over nickel resulted in the cleavage of one oxygen to carbon linkage with the formation of ethers.[3] However, it has been found possible to avoid this reaction in considerable part during the hydrogenation of the diethyl acetal of furfural. The ratio of products is, however, dependent upon the purity of the acetal and of the character of the catalyst. The competitive reactions involved are illustrated in equations I and II.



(I)



(II)

There is also produced resinous material of unknown composition.

There is recorded in Table III a summary of more significant data obtained during the course of an extensive study of the hydrogenation of diethyl furfural acetal. The variations in the proportion of the products for a sodium carbonate catalyst (15), a bicarbonate catalyst (44) and for an ammonium carbonate catalyst (24) are given at the top of the tabulation. It was suspected that the reason that catalyst 15 produced the hydrogenated acetal in a yield of 43% while catalysts 24 gave only 11% was because of the (probable) alkali content of the former. Therefore 0.5 g. of sodium carbonate was added to a sample of the latter catalyst and the mixture tested in the hydrogenation of the acetal. The hydrogenation

[3] Sigmund and Marchart, *Monatsh.*, **48**, 267 (1927); Sigmund and Uchann, *ibid.*, **51**, 234 (1929); and Cabanac, *Compt. rend.*, **188**, 1257 (1929).

was very much slower but the yield of saturated acetal was raised to 44%, a yield which is practically identical with the best previous yield with catalyst

TABLE III

HYDROGENATION OF THE ETHYL ACETAL OF FURFURAL

| Catalyst G. | Catalyst No. | Moles acetal | Added material, g. | | Moles $H_2$ | Hrs. at 175° | Ethyl tetrahydrofurfuryl ether[g] | Ethyl tetrahydrofurfural acetal[h] | Residue |
|---|---|---|---|---|---|---|---|---|---|
| 4 | 15[a] | 0.74[e] | ... | ..... | 1.84 | 7.5 | 18 | 45 | 16 |
| 4 | 44[b] | .3 | ... | ..... | 0.75 | 0.2 | 60 | 5 | 13 |
| 2 | 24[c] | .3[e] | ... | ..... | .93 | 0.0 | 61 | 11 | 10 |
| 2 | 24[c] | .3 | 0.5 | $Na_2CO_3$ | .90 | 4.0 | 12 | 44 | 14 |
| 2 | 24[c] | .3 | .2 | Furoic acid | .87 | 1.5 | 31 | 30 | 14 |
| 4 | 24[c,d] | .3 | .1 | NaOH | .81 | 4.0 | 13 | 59 | 13 |
| 4 | 24[c,d] | .7 | .2 | NaOH | 2.28 | 8.0 | 6 | 71 | 12 |
| 2 | 24[c] | .3 | .01 | $NaOC_2H_5$ | 0.82 | 0.05 | 17 | 41 | 9 |
| 4 | 24[c] | .65 | .5 | Piperidine | 1.95 | 2.8 | 5 | 51 | 17 |
| 3 | 24[c] | .3 | .5 | Cyclohexylamine | 0.80 | 1.8 | 21 | 48 | 14 |
| 3 | 24[c] | .3 | .5 | Di-*n*-amylamine | .76 | 0.33 | 14 | 63 | 9 |
| 3 | 24[c] | .3 | .5 | *n*-Amylamine | .76 | .16 | 6 | 74 | 9 |
| 3 | 24[c] | .3 | .5 | α-Methylpiperidine | .79 | .25 | 10 | 62 | 9 |
| 3 | 24[c] | .3 | .5 | *n*-Butylamine | .83 | .20 | 5 | 75 | 9 |
| 3 | 24[c] | .3 | .5 | N-Cyclohexylpiperidine | .76 | .15 | 5 | 75 | 9 |
| 3 | 24[c] | .3 | 1.0 | *n*-Amylamine | .82 | .13 | 5 | 75 | 10 |
| 3 | 24[c] | .3 | 0.5 | β-Phenylethylamine | .77 | .30 | 4 | 75 | 13 |
| 3 | 15[a] | .3 | .5 | *n*-Amylamine | .83 | .66 | 9 | 63 | 11 |
| 2 | 44 + Cu[f] | .3 | .5 | *n*-Amylamine | .67 | .6 | 4 | 76 | 9 |
| 2 | 44 + Ce[f] | .3 | .5 | *n*-Amylamine | .67 | .1 | 33 | 28 | 9 |
| 2 | 44 + Fe[f] | .3 | .5 | *n*-Amylamine | .75 | .25 | 15 | 58 | 11 |

[a] Sodium carbonate was added as a precipitant to the nickel nitrate on kieselguhr.

[b] Sodium bicarbonate was added as a precipitant to the nickel nitrate on kieselguhr.

[c] The nickel nitrate on kieselguhr was added to ammonium carbonate solution as a precipitant.

[d] Two applications of catalysts were necessary.

[e] These samples of acetal were not of the same lot as used in testing catalysts 24 and 44.

[f] These catalysts were prepared as was No. 44, *i. e.*, by the use of $NaHCO_3$ as a precipitant as in *b* above, and in addition contained the indicated element in the ratio of 1 part of it to approximately 9 parts of nickel.

[g] This fraction was taken 47 to 55° (11 mm.). Ethyl tetrahydrofurfuryl ether was reported by Kirner [THIS JOURNAL, **52**, 3251 (1930)] to have a boiling point 152–154° (726 mm.).

[h] This fraction was taken 76 to 80° (11 mm.). The diethyl acetal of tetrahydrofurfural was reported by Scheibler, Sotscheck and Friese [*Ber.*, **57**, 1443 (1924)] to have a boiling range of 187–190°. Bolander and Minne in this Laboratory have found the boiling point of the pure compound to be 194.5°.

15. Sodium hydroxide (0.2 g.) was even more effective in increasing the yield of the acetal, although the rate of hydrogenation was so decreased that it was necessary to open the bomb and add a second sample of catalyst in order to complete the hydrogenation. Unfortunately for the hypothesis that the increased yield of acetal was due to the alkali, it was found that the addition of furoic acid to the reaction mixture had a similar but not so great beneficial effect as the bases.

The most effective reagents for increasing the yield of acetal are the amines. A number of them were tried as indicated in Table III, the most effective being *n*-amyl, *n*-butyl and β-phenylethylamines, and N-cyclohexylpiperidine. The addition of 0.5 g. of *n*-amylamine to 50 g. of the acetal made it possible to obtain 75% of the theoretical yield of the saturated acetal. This is to be contrasted with the yield of 11% in the absence of the amine, or of 43% with the sodium carbonate catalyst.

Mr. Nels Minné in this Laboratory has had occasion during recent months to use this process for the preparation of considerable quantities of diethyl tetrahydrofurfural acetal. He has consistently obtained approximately 220 g. of the saturated acetal by hydrogenating 280 g. (1.65 moles) of diethyl furfural acetal, containing 1.0 g. of *n*-amylamine, with 8 g. of an ammonium carbonate type of nickel catalyst in five hours at 200 atmospheres. This represents an actual yield of 76% of the theoretical or 80% if allowance is made for the mechanical losses.

The amines are also effective as shown in the table in increasing the yield of acetal for the sodium carbonate and sodium bicarbonate catalysts and for bicarbonate catalysts containing copper, cerium and iron although in the case of the latter two the yield of acetal was considerably lower than for the other catalysts. It is significant that the amines which are so effective in modifying the ratio of the products accomplish this without any considerable decrease in the *rate* of hydrogenation. As has been repeatedly emphasized in publications from this Laboratory, there is no necessary relationship between the activity of a catalyst and the proportion of the competitive reactions produced over it.

In a similar way the addition of 0.2 g. of *n*-amylamine doubled the yield of cyclohexylcarbinol (see Table IV) formed in the reduction of 25 g. of benzyl alcohol over an ammonium carbonate catalyst. However, no catalyst has been prepared which was more effective in producing cyclohexylcarbinol than are those prepared by the original sodium carbonate method. This is also true for the production of methylphenylcarbinol from acetophenone (Table IV), for which the carbonate type of catalyst was the most effective. Another interesting observation in this connection is that catalyst 8 gave only one-third as much of the carbinol when the catalyst had been reduced at 575° as when it was reduced at 450°.

## TABLE IV

### HYDROGENATION OF VARIOUS COMPOUNDS

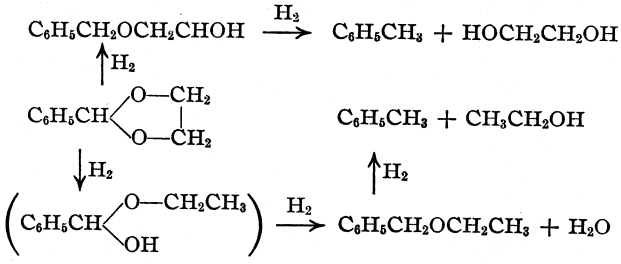
| Compound Name | Mole | $H_2$, moles, | Time, hrs. | Temp., °C. | Pressure, atm. | Catalyst[k] G. | No. | Solvent, ml. | % | Products and yields |
|---|---|---|---|---|---|---|---|---|---|---|
| Benzilidene ether of ethylene glycol (118–20° (22 mm.) | 0.29 | 0.9 | 6.5 | 125 | 125 | 2 | 9 | .... | 31 | Toluene, ethanol and loss[d] |
| | | | | | | | | | 21 | Ethylene glycol and benzyl ethyl ether (96–106°) (24 mm.)[e] |
| | | | | | | | | | 48 | Monobenzyl ether of ethylene glycol (132–144°) (22 mm.)[f] |
| Benzyl ether of ethylene glycol | .1 | .. | 2.0 | 175 | 125 | 2 | 9 | 35 Ether | 53 | Methylcyclohexane and loss[d] |
| | | | | | | | | | 25 | Ethylene glycol |
| | | | | | | | | | 22 | Hexahydrobenzyl ether of ethylene glycol (123.5–125.5°) (25 mm.)[g] |
| Benzyl ethyl ether[i] | .31 | .. | 0.5 | 175 | 120 | 3 | 16 | .... | 37 | Cleavage of the ether to toluene and ethanol. Complete cleavage on reapplication of catalyst |
| Benzilidene ether of ethylene glycol[e] | .33 | .. | 4.5 | 175 | 120 | 3 | 24 | .... | 53 | Ethylene glycol |
| | | | | | | | | | 41 | Toluene and methylcyclohexane[h] |
| | | | | | | | | | 12 | Benzyl ethyl ether[h] |
| | | | | | | | | | 21 | β-Hydroxyethyl benzyl ether[h] |
| Benzilidene ether ethylene glycol | .33 | 0.84 | 2.0 | 175 | 120 | 6[a] | 24 | .... | 86 | Glycol |
| | | | | | | | | | 80 | Hydrocarbons[h] |
| Benzilidene ether of trimethylene glycol[i] (137–138) (22 mm.) | .31 | 1.3 | 4.5 | 175 | 120 | 3 | 24 | .... | 87 | Trimethylene glycol |
| | | | | | | | | | 67 | Hydrocarbons[h] |
| | | | | | | | | | 10 | Ethers[h] |
| Benzilidene ether of trimethylene glycol and 0.5 g. of *n*-amylamine | .31 | 1.3 | 8.0 | 175 | 120 | 6[a] | 24 | .... | 54 | Trimethylene glycol |
| | | | | | | | | | 56 | Hydrocarbons[h] |
| | | | | | | | | | 34 | Ethers[h] |
| 1,2-Benzilidene ether of glycerol | .25 | 0.70 | 4.0 | 175 | 120 | 6[a] | 24 | .... | 80 | Glycerol, 70% hydrocarbons[h], 14% of other products |
| Dimethylaniline | .83 | 2.46 | 5 | 185 | 102 | 3 | 1 | .... | 95 | Dimethylcyclohexylamine, (50.8–51.5° (15 mm.)), 3.5 g. (53–71° (15 mm.)) 1.5 g. residue |
| { Benzyl acetate<br>{ Dimethylcyclohexylamine | .33<br>.37 | 0.33 | 5 | 135 | 123 | 3 | 1 | .... | 100 | Cleavage to toluene and acetic acid |
| Benzalacetone[i] | .50 | .59 | 0.03 | 45–87 | 122 | 3 | 5 | 57 EtOH | 96 | Benzyl acetone (130–133 (15 mm.)) |
| Mesityl oxide | .33 | .33 | 1 | 125 | 120 | 2 | 15 | .... | 95–100 | Methyl isobutyl ketone (114–116° (740 mm.)) |
| Methyl isobutyl ketone (contained the carbinol) | .39 | .. | 3 | 150 | 120 | 2 | 15 | .... | 95–100 | Methylisobutylcarbinol (130–131° (740 mm.)) |
| Catechol | .22 | .68 | 4 | 175 | 120 | 4 | 15 | 30 EtOH | 95–100 | *Cis* and *trans* cyclohexanediol-1,2 (119–122 (10 mm.)) (cryst. from ether, m. p. 71–72°) |
| Ethyl levulinate[i] | .21 | .. | 1.4 | 100 | 120 | 4 | 15 | .... | 85 | Ethyl γ-hydroxyvalerate (84–85° (3 mm.)) |
| Nitrobenzene | .50 | .. | 1.1 | 100 | 120 | 4 | 16 | 50 EtOH | 95–100 | Aniline (182–186° (740 mm.)) |
| *m*-Dinitrobenzene | .25 | .. | 1.12 | 100–110 | 120 | 2 | 15 | 50 Ether | 95–100 | *m*-Diaminobenzene (153–154° (10 mm.)) |
| N-methyl α-pyridone[i] | 1.24 | 2.48 | 1.33 | 100 | 120 | 2 | 15 | .... | 95–100 | 1-Methyl-2-piperidone (97–98° (11 mm.)) |

TABLE IV (*Concluded*)

| Compound Name | Mole | $H_2$, moles, | Time, hrs. | Temp., °C. | Pressure, atm. | Catalyst[k] G. | No. | Solvent, ml. | % | Products and yields |
|---|---|---|---|---|---|---|---|---|---|---|
| *o*-Hydroxybenzaldehyde | 0.20 | 0.31 | 1.00 | 75 | 120 | 2 | 15 | .... | 57 | *o*-Hydroxybenzyl alcohol (m. p. 85–86° from benzene) |
| | | | | | | | | | 26 | *o*-Cresol |
| Ethyl formyl phenoxy acetate[i] | .04 | .. | 0.1 | 110 | 100 | 2 | 13 | 40 EtOH | | Ethyl α-phenoxyhydrocrylate (168–170° (10 mm.)) |
| Glucose | .11 | .. | 2.5 | 150 | 170 | 2 | 17 | 35 $H_2O$ (or ether) | 97 | Sorbitol |
| Fructose | .11 | .. | 2.5 | 150 | 170 | 2 | 17 | 25 $H_2O$ | 97 | Mannitol (m. p. 127–132°) |
| Glucose | .11 | .. | 4.0 | 160 | 170 | 1 | Cu–Cr | 60 95% EtOH | 97 | Sorbitol |
| Benzalacetophenone | .36 | .. | 0.1 | 65 | 125 | 3 | 13 | 80 EtOH | 90–95 | Phenyl β-phenylethyl ketone |
| Ethyl benzoate[i] | 2.09 | .. | 1.0 | 190–250 | 200 | 8 | 4 | .... | 95–100 | Ethyl hexahydrobenzoate (84–86° (16 mm.)) |
| Acetophenone | 0.40 | 0.77 | 0.33 | 175 | 120 | 2 | 16 | .... | 10 | Methylphenylcarbinol |
| | | | | | | | | | 84 | Ethylcyclohexane |
| Acetophenone | .40 | .84 | .16 | 175 | 120 | 2 | 15 | .... | 30 | Methylphenylcarbinol |
| | | | | | | | | | 65 | Ethylcyclohexane |
| Acetophenone | .40 | .86 | .40 | 175 | 120 | 2[b] | 8 | .... | 25 | Methylphenylcarbinol |
| | | | | | | | | | 70 | Ethylcyclohexane |
| Acetophenone | .40 | .83 | .10 | 175 | 120 | 2[c] | 8 | .... | 8 | Methylphenylcarbinol |
| | | | | | | | | | 88 | Ethylcyclohexane |
| Benzyl alcohol | .23 | .30 | .16 | 125 | 120 | 2 | 24 | .... | 8 | Cyclohexylcarbinol |
| | | | | | | | | | 88 | Toluene |
| Benzyl alcohol | .23 | .30 | .40 | 125 | 120 | 2 | 24 | .... | 16 | Cyclohexylcarbinol |
| 0.2 g. *n*-Amylamine | | | | | | | | | 78 | Toluene |
| Hydrofurfuramide[l] | | | | | | | | | | |

[a] Two applications of 3 g. each of catalyst were necessary for the hydrogenation. [b] The catalyst was reduced 0.75 hr. at 450°. [c] The catalyst was reduced 1.0 hr. at 575°. [d] The loss of the more volatile components was high because of the difficulty of filtering off the catalyst and therefore the yields are not given as percentage of the theoretical yield, but represent the distribution of the weights of the various products. [e] These two compounds were separated on the basis of their solubility in water. A dibenzoate of the glycol was made of m. p. 68–70°, and the ether characterized by its boiling point and its inertness toward the ordinary alcoholic reagents. [f] The benzyl ether of ethylene glycol was characterized by its boiling point (138° (15 mm.)) [Bennett, *J. Chem. Soc.*, **127**, 1277 (1925)], and by its urethan from α-naphthyl isocyanate, m. p. 89–90°. [g] The hexahydrobenzyl ether of ethylene glycol gave a urethan with α-naphthol isocyanate, m. p. 57–58.5°. The compound was analyzed by Mr. E. F. Struss. Calcd. for $C_9H_{18}O_2$: H, 11.39; C, 68.37. Found: H, 11.40; C, 68.40. [h] The benzenoid rings were no doubt partially hydrogenated. [i] The losses in these experiments were nominal (5%), as the water-soluble layer was separated from the hydrocarbon layer before filtering. Alcohol was then added to the glycol layer so that the filteration could be expedited and losses minimized. [j] These compounds were hydrogenated in collaboration with Messrs. E. A. Prill, Ralph Thomas, E. F. Struss, C. F. Koelsch, George Pfeiffer or Karl A. Folkers. [k] Ammonium carbonate was used as the precipitant in the preparation of catalysts 23, 24 and 37, sodium bicarbonate was used for catalysts 4, 5, 9, 16, 17 and 44, while the sodium carbonate A method was used for catalysts 1, 8, and 13 and the B method for 15 (see reference 1 for details of these preparations). [l] Hydrofurfuramide upon hydrogenation over nickel behaves similarly to hydrobenzamide in that at 80° it was converted in more than 90% yield to an easily separated equimolecular mixture of mono- and di-tetrahydrofurfuryl amines.

**Cyclic Acetals.**—In an attempt to protect the carbonyl group during hydrogenation of the benzene nucleus in the presence of nickel, cyclic acetals of benzaldehyde with ethylene glycol, trimethylene glycol and glycerol were prepared. A summary of experimental results obtained in the hydrogenation of these acetals is given in Table IV. In the hydrogenation, cleavage of oxygen to carbon linkages always occurred and no traces of the saturated cyclic acetal could be found. The ease of cleavage of an oxygen linkage on a carbon atom attached to a benzenoid ring has been noted by various investigators.[4] The course of the hydrogenation of a cyclic acetal (benzilidene ether of ethylene glycol) may be represented as below




The scheme presupposes that the cleavage of oxygen to carbon linkages in the acetal occurs between the oxygen to methylene as well as between the oxygen to methine group. The above scheme accounts for the products obtained at 125°, *i. e.*, toluene, ethylene glycol, benzyl ethyl ether and the monobenzyl ether of ethylene glycol. At 175° these same products were obtained accompanied by the corresponding hexahydro compounds. Ethylene glycol and hydrocarbons were obtained at 175° from the benzyl ether of ethylene glycol. The hydrogenation of the benzilidene ether of trimethylene glycol and of the 1,2-benzilidene ether of glycerol yielded results similar to those obtained from the ether of ethylene glycol except that the hydrogenation proceeded more slowly.

It should be noted that there is a rather important difference between the hydrogenation of the cyclic acetals and that of furfural acetal or benzyl alcohol. In the case of these latter compounds the hydrogenation proceeded smoothly to a definite limit and the proportion of products was determined by the catalyst and not by the duration of the hydrogenation. In the case of the cyclic acetals the proportion of the products appears to be primarily determined by the duration of the hydrogenation and little, if any, by the presence of an amine or by the type of catalyst used for the hydrogenation. If the hydrogenation were allowed to go as long as hydrogen was absorbed, then ethanol, glycol and toluene were the only products. If the reaction were stopped at an earlier stage, then the ether alcohol, and the ether were found among the products.

[4] *Cf.* Adkins and Cramer, THIS JOURNAL, **52**, 4349 (1930).

**Other Hydrogenations.**—There is recorded in Table IV a summary of the results obtained in the hydrogenation of a variety of organic compounds. The chief significance, for the present, of these results lies in the establishment of experimental conditions under which these compounds may be hydrogenated in good yield so that it is unnecessary to discuss them in detail. It will suffice to point out a few matters of importance.

In certain hydrogenations acids are produced which attack the nickel. It is desirable to have available a base that may be introduced into the hydrogenation mixture which will neutralize the acid and yet not poison the catalyst as would aniline or sodium hydroxide, for example. Dimethylcyclohexylamine has proven to be such a base. For example, the addition of the tertiary amine to benzyl acetate permitted the complete hydrogenation. Cramer[4] found that in the absence of the amine the hydrogenation stopped due to the solution of the nickel in acetic acid.

The hydrogenation of benzal acetone, benzalacetophenone and mesityl oxide illustrates the feasibility of converting an unsaturated ketone into a saturated ketone by hydrogenation over nickel if the catalyst is sufficiently active to permit the hydrogenation to be carried out at a low temperature.

The rapid and almost quantitative hydrogenation of nitrobenzene and *m*-dinitrobenzene in alcohol to the corresponding amines indicates the practicability of this process. Without a solvent an immiscible layer was formed and the hydrogenation was unsuccessful. All attempts to produce *m*-nitroaniline from *m*-dinitrobenzene were unsuccessful. It should be noted that the hydrogenation of a nitro group is a very exothermic process so that the rate of hydrogenation must be carefully controlled in order to avoid so rapid a reaction that the temperature becomes excessively high. The rate of hydrogenation is determined by the ratio of catalyst to nitro compound, the temperature and pressure of hydrogen and especially by the rate of shaking of the bomb.[5]

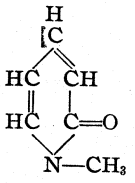
The smooth hydrogenation of the alkene linkage of ethyl formyl phenoxyacetate ($HOCH{=}C(OC_6H_5)COOC_2H_5$) to ethyl $\alpha$-phenoxyhydracrylate ($HOCH_2CH(OC_2H_5)COOC_2H_5$) is significant in view of the fact that Koelsch found several other methods to result in failure due to cleavage of the molecule.[6]

The excellent results obtained in the hydrogenation of N-methyl-$\alpha$-pyridone (A), to 1-methyl-2-piperidone (B) are worthy of note in view of the slowness of the hydrogenation of this compound over various platinum catalysts.[7]

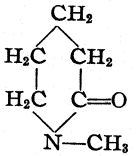
[5] Adkins, THIS JOURNAL, **53**, 2808 (1931).

[6] Koelsch, *ibid.*, **52**, 2435 (1930).

[7] Ruzicka, *Helv. Chim. Acta*, **4**, 474 (1921); Ruzicka, Seidel and Leiff, *ibid.*, **7**, 1002 (1924); Graves, THIS JOURNAL, **46**, 1470 (1924); Prill and McElvain, unpublished work from this Laboratory with Adams' catalyst.



(A)



(B)

Glucose was successfully hydrogenated in the presence of a nickel or of copper–chromium oxide catalyst in ethanol, ether or water as a reaction media. Fructose could be hydrogenated by the use of nickel but copper–chromium oxide caused decomposition. The temperature of the reaction mixture should be kept below 160° in order to avoid decomposition. The completeness of hydrogenation of glucose to sorbitol was shown by the fact that the $(\alpha)_D^{25}$ for the product ranged from 0.0 to + 1.6. The mannitol produced from fructose evidently contained a small percentage of sorbitol for the product although crystalline melted at 127–132° instead of 166°.

## Summary

A study of the preparation of nickel catalysts has shown that the amount of nickel held by the support and the proportion of the nickel compounds which are reducible to metallic nickel are a function of the precipitant and procedure of precipitation, as is also the optimum time and temperature for the reduction of the nickel oxides to the active catalyst. On the basis of this and previous investigations a procedure has been recommended which results in easily reproducible and very active nickel catalysts.

The incorporation of several different elements into the nickel catalyst promoted the hydrogenation of toluene, acetone and of the diethyl acetal or furfural. These so-called promoters are so specific in their action that an element that promotes the hydrogenation of one compound may inhibit that of another.

It has been found possible through the addition of various substances, especially of certain amines, to so control the hydrogenation of diethyl furfural acetal as to raise the yield of diethyl tetrahydrofurfural acetal from a few per cent. to 75–80% of the theoretical, there being a corresponding decrease in the yield of ethyl tetrahydrofurfuryl ether. The addition of *n*-amylamine had a similar but smaller effect in increasing the yield of cyclohexylcarbinol from benzyl alcohol.

Three cyclic acetals of benzaldehyde were subjected to hydrogenation under various conditions but in no case was there any evidence for the formation of hexahydrobenzaldehyde or its acetals. The products were hydrocarbons, ethers, hydroxy ethers and glycols.

Suitable experimental conditions have been established for the successful

hydrogenation of a variety of organic compounds as summarized in the paragraphs in "Other Hydrogenations" and in Table IV.

MADISON, WISCONSIN

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[CONTRIBUTION FROM METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

# ALIPHATIC GERMANIUM DERIVATIVES. II. DIETHYLDIPHENYLGERMANE, DIETHYLGERMANIUM OXIDE AND DIETHYLGERMANIUM DIBROMIDE

BY E. A. FLOOD

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## I. Introduction

A study of the triphenyl,[1,2] diphenyl[1,3] and triethylgermanium[4] compounds has revealed some interesting contrasts in the chemistries of these little known amphoteric groups. Continuing the study of this class of substances some diethylgermanium derivatives have been isolated and some of their properties determined. It has been found convenient in previous work to use the halide of the group under investigation as the source of subsequent derivatives. Accordingly, the first objective in this research was the preparation and study of diethylgermanium dibromide. The most satisfactory method of preparing this compound involved bromination of triethylgermanium fluoride,[4] hydrolysis of the product and conversion of the resulting diethylgermanium oxide, after purification, into the corresponding bromide.

Diphenylgermanium dibromide can be prepared by the action of bromine on tetraphenylgermane[5] and while it might be expected that diethylgermanium dibromide, $(C_2H_5)_2GeBr_2$, could be prepared by the analogous reaction of bromine on tetraethylgermane, this has not been found feasible. All attempts to substitute a second bromine atom for an ethyl group in triethylgermanium bromide by the direct action of bromine gave complex mixtures from which only very low yields of diethylgermanium dibromide could be obtained.

Some preliminary experiments indicated that diethylgermanium dibromide can be prepared by an indirect method starting with diphenylgermanium dibromide. The diphenylgermanium dihalide was treated with ethylmagnesium bromide and the resulting diphenyldiethylgermane on bromination gave impure diethylgermanium dibromide.

[1] Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1927).

[2] Kraus and Foster, THIS JOURNAL, **49**, 457 (1927).

[3] Kraus and Brown, *ibid.*, **52**, 3690 (1930).

[4] Kraus and Flood, *ibid.*, **54**, 1635 (1932).

[5] Kraus and Brown, *ibid.*, **52**, 3690 (1930). $(C_6H_5)_2GeBr_2$ was obtained by Morgan and Drew[1] from the reaction of $GeBr_4$ with $C_6H_5MgBr$. Partial ethylation of $GeBr_4$ by $C_2H_5MgBr$ yields $(C_2H_5)_3GeBr$ but little or no $(C_2H_5)_2GeBr_2$.[4]

Since diphenyldiethylgermane has hitherto not been described in the literature its preparation and properties will be discussed briefly.

## II. Diphenyldiethylgermane, $(C_6H_5)_2Ge(C_2H_5)_2$

When trimethylphenylstannane is treated with bromine the phenyl group is substituted preferentially.[6] It seemed probable, therefore, that similar preferential substitution would occur in the case of diphenyldiethylgermane, yielding diethylgermanium dibromide and phenyl bromide. Accordingly diphenyldiethylgermane was prepared and brominated. The experimental details appear in the following paragraphs.

**Preparation.**—Diphenyldiethylgermane was prepared by means of the Grignard reaction, using diphenylgermanium dibromide and ethylmagnesium bromide. The yield obtained was about 95% of the theoretical.

A solution of 11.7 g. of diphenylgermanium dibromide in 50 cc. of ether was slowly added to 200 cc. of an ether solution of ethylmagnesium bromide equivalent to 10 g. of ethyl bromide. During the reaction the mixture was cooled by means of an ice-bath and vigorously stirred. The mixture was heated to boiling for a period of three hours, after which the ether was removed by distillation and the residual mass heated to a temperature of 110° for three hours. After cooling the mixture the excess Grignard reagent was hydrolyzed and the product extracted with ether. The extract was dried over calcium chloride, the ether removed and the residual liquid subjected to vacuum distillation; 8.3 g. of a colorless liquid boiling at 316° (uncorr.) under atmospheric pressure was obtained corresponding to a yield of 96%. The product was further purified by slow fractional distillation and the purity of the product which distilled between 315–317° (uncorr.) tested by analysis. Analyses were carried out by a modified Krause method.[4,7]

*Anal.* Subs., 0.3495, 0.2364: $GeO_2$, 0.1288, 0.0869. Calcd. for $(C_6H_5)_2Ge(C_2H_5)_2$: Ge, 25.50. Found: Ge, 25.58, 25.51, mean, 25.55.

**Properties.**—Diphenyldiethylgermane is a colorless liquid having a rather pleasant odor and boiling at 316° (uncorr.) at atmospheric pressure. It is insoluble in water but miscible with organic solvents. This compound is quite stable toward air and moisture and may be boiled in air without appreciable decomposition; however, it reacts readily with bromine in ethylene dibromide solution.

**Bromination.**—A solution of 1.44 g. of diphenyldiethylgermane in 5 cc. of ethylene dibromide was treated with successive portions of a solution of bromine in ethylene dibromide containing 0.76 g. of bromine per cc. of solution. In all 1.62 g. of bromine was added. The first half of the bromine reacted readily in the cold while the second half was consumed only after heating to 100° for twelve hours. On completion of the reaction, the mixture was fractionally distilled, three distinct fractions being obtained. The first was identified as ethylene dibromide, a small second fraction was found to be largely phenyl bromide and the third, amounting to 1.3 g. which was collected between 199–205° consisted of diethylgermanium dibromide, $(C_2H_5)_2GeBr_2$ (b. p. 202°).

The chief products of brominating diphenyldiethylgermane were those anticipated, thus indicating a method of preparing diethylgermanium dibromide. However, a more direct method of preparation was developed starting with triethylgermanium derivatives rather than the phenyl compound.

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[6] Bullard and Robinson, THIS JOURNAL, **49**, 1368 (1927).

[7] Krause, *Ber.*, **55**, 896 (1922).

The above experiment suggests that the regularities previously observed on the bromination of alkyl-aryl-tin[8] compounds may apply to the corresponding germanium derivatives.

## III. Diethylgermanium Oxide, $(C_2H_5)_2GeO$

An experiment on the relative rates of reaction of bromine with triethylgermanium fluoride, chloride and bromide, showed that reaction occurred about six times more rapidly with the fluoride than with the chloride and with the chloride, in turn, six times more rapidly than with the bromide. Moreover, it was observed that while the reaction of bromine with triethylgermanium bromide yielded considerable quantities of hydrogen bromide, no detectable hydrogen bromide was evolved when the fluoride was brominated under similar conditions. These observations led to a satisfactory method of preparing diethylgermanium derivatives, wherein triethylgermanium fluoride was brominated and the crude diethylgermanium dihalides converted, by hydrolysis, into diethylgermanium oxide. It may be pointed out that a good deal of difficulty was at first encountered in obtaining a pure product because of the proximity of the boiling points of the various ethylgermanium halides and the apparent lack of definite physical properties of diethylgermanium oxide. The peculiar properties of the oxide were found to be due to polymerization and, taking advantage of these properties, a very convenient method of purification was developed.

**Bromination of Triethylgermanium Fluoride, $(C_2H_5)_3GeF$.**—Triethylgermanium fluoride was treated first with a concentrated solution of bromine in ethyl bromide and subsequently with two portions of pure bromine, the bromine additions being made after the previously added bromine had been consumed. In all about 5% excess of one mole of bromine per mole of fluoride was used. The bromination was carried out at a temperature of 50° except during the final stage of the reaction, when the mixture was heated to boiling. Carefully dried materials were used and precautions taken to exclude moisture during the reaction, which extended over a period of about three days. When reaction was judged to be complete, the mixture was hydrolyzed by heating with an aqueous solution of sodium hydroxide. The hydrolyzed product was extracted with ether and the ethereal solution dried over anhydrous sodium sulfate.

When the residual aqueous solution was acidified, a relatively small quantity of a white solid was precipitated. Analysis of this substance for germanium indicated impure ethylgermanic acid (calcd. for $C_2H_5GeOOH$: Ge, 53.9; found: Ge, 55.6).

Fractional distillation of the ethereal extract yielded a high boiling liquid—collected in three consecutive portions—which distilled in the vicinity of 285° but gave little indication of a definite boiling point. The three samples obtained were liquid and of a bluish "fluorescent" color. After standing for four hours the first solidified to a white mass. The other two samples remained liquid after standing several days; however, when a trace of water was added, they also solidified within a few hours.

The solidified product was found to be insoluble in ether and consequently the three solid samples were combined, pulverized and the soluble impurities extracted with ether in a Soxhlet extractor. Since the product had been extracted previously from the

[8] Bullard, THIS JOURNAL, **51**, 3065 (1929).

hydrolyzing solution with ether, ether-insoluble impurities were largely absent. The insoluble residue was distilled at a temperature of 160° under a pressure of 0.01 mm. A crystalline product was obtained which melted sharply at 18°. After standing for twelve hours in a sealed tube the product had changed into a white amorphous solid melting at about 175° when heated rapidly, but which liquefied slowly when maintained at a temperature of 120°. The liquid yielded crystals melting at 19° but solidified again on standing at room temperature.

This material was shown by analysis to be diethylgermanium oxide. The first sample used for analysis was of the liquid form, the second was taken shortly after solidification, the third a solid sample which had been exposed to the air for nine days and the fourth a sample from another preparation which had been exposed for several weeks.

*Anal.* Subs., 0.1809, 0.2471, 0.2383, 0.0921: $GeO_2$, 0.1288, 0.1766, 0.1704, 0.0658. Calcd. for $(C_2H_5)_2GeO$: Ge, 49.49. Found: Ge, 49.42, 49.60, 49.63, 49.59.

**Properties of Diethylgermanium Oxide.**—Diethylgermanium oxide exists in two polymeric forms. At room temperature the stable form is a white amorphous solid melting at about 175° when heated rapidly. It is insoluble in organic solvents, water and liquid ammonia. The oxide also exists in an unstable liquid form which crystallizes at 18° (approx.). In this form diethylgermanium oxide is soluble in organic solvents, but insoluble in water and in liquid ammonia.

That the unstable, soluble form is trimolecular is shown by the following data: mol. wt. (cryoscopic method). Subs., 0.3221, 1.1437; $C_6H_6$, 16.226, 16.226; $\Delta t$, 0.218, 0.758. Calcd. for $[(C_2H_5)GeO]_3$: mol. wt., 440. Found: mol. wt., 455, 465, mean, 460.

Transformation of the liquid to the solid form at room temperature occurs within a few hours and is accelerated by the presence of a trace of water while transition between the two forms occurs in the vicinity of 110°.

When treated with a concentrated aqueous solution of halogen acid, diethylgermanium oxide is converted to the corresponding diethylgermanium dihalide. The oxide reacts readily, with lithium in ethylamine solution but is fairly stable toward oxidation, no sign of decomposition occurring when it is heated to 290° in air.

## IV. Diethylgermanium Dibromide, $(C_2H_5)_2GeBr_2$

**Preparation.**—Diethylgermanium dibromide was prepared by shaking pure diethylgermanium oxide with a concentrated aqueous solution of hydrobromic acid. After allowing the mixture to stand overnight the resulting diethylgermanium dibromide was extracted with petroleum ether, the petrol solution dried over calcium chloride and finally fractionally distilled. The fraction which distilled between the thermometer readings 201.5–202° was subjected to vacuum distillation and the final product analyzed for germanium and bromine. The germanium in the compound was determined as germanium oxide by the usual modified Krause method while the bromine was determined by hydrolyzing the sample with an aqueous solution of sodium hydroxide, filtering the mixture and determining the bromine in the aqueous filtrate as silver bromide.

*Anal.* Subs., 0.3168, 0.2342: AgBr, 0.4089, 0.3029. Calcd. for $(C_2H_5)_2GeBr_2$: Br, 55.02. Found: Br, 54.93, 55.04, mean, 54.99. Subs., 0.2651, 0.2142: $GeO_2$, 0.0954, 0.0770. Calcd.: Ge, 24.99. Found: Ge, 24.98, 24.95, mean, 24.97.

**Properties.**—Diethylgermanium dibromide is a colorless liquid having a sharp odor, suggestive of hydrogen chloride. It boils at 202° (uncorr.) under atmospheric pressure but fails to solidify when cooled to −33°. When treated with water or aqueous alkaline solutions the bromide is hydrolyzed, forming diethylgermanium oxide. Similarly, with liquid ammonia ammonolysis occurs, as will be shown below, yielding diethylgermanium imine, $(C_2H_5)_2GeNH$.

**Ammonolysis of Diethylgermanium Dibromide.**—Preliminary experiments, in which weighed samples of diethylgermanium dibromide were treated with ammonia, indicated that three molecules of ammonia enter into reaction with one molecule of the dibromide, thus suggesting that ammonolysis occurs according to the equation

$$(C_2H_5)_2GeBr_2 + 3NH_3 = (C_2H_5)_2GeNH + 2NH_4Br \quad (1)$$

The results were confirmed by isolating the amino derivative and determining its composition.

A sample of the dibromide was placed in a special reaction tube, designed to permit adequate stirring of the reaction mixture and equipped also with a side vessel into which the product of the reaction could be distilled and the distillate collected in fragile glass bulbs. Liquid ammonia was condensed into the reaction tube and the mixture stirred vigorously during several hours. On addition of sodium, a vigorous reaction ensued with evolution of hydrogen, indicating the presence of ammonium bromide formed by ammonolysis. Reaction was complete after three days when a permanent blue color, due to excess sodium, was obtained. The excess ammonia was now removed and the product distilled into the collecting chamber containing the fragile bulbs, the distillation being carried out under a pressure of 0.01 mm. The bulbs were filled with the distillate and sealed in an atmosphere of dry nitrogen.

The product was analyzed for nitrogen by breaking a bulb, containing a weighed sample of the amino derivative, under a known volume of dilute standard acid and allowing the well shaken mixture to stand overnight. Titrating the excess acid with standardized sodium hydroxide solution gave indirectly the ammonia formed by hydrolysis of the amino derivative.

*Anal.* Subs., 0.1170, 0.1033: cc. of 0.07044 *N* HCl, 11.12, 9.97. Calcd. for $(C_2H_5)_2GeNH$: N, 9.61. Found: N, 9.38, 9.52, mean, 9.45.

Analyses indicate that the product is diethylgermanium imine, thus establishing equation (1).

**Properties of Diethylgermanium Imine $(C_2H_5)_2GeNH$.**—Diethylgermanium imine is a colorless liquid which distils when heated to 100° under a pressure of 0.01 mm. It hydrolyzes very easily, being decomposed rapidly on exposure to air, with the liberation of ammonia and the formation of diethylgermanium oxide. A molecular weight determination gave 394, while that calculated for $(C_2H_5)_2GeNH$ is 146, indicating that the imine is polymerized.

## V. Summary

1. Diphenyldiethylgermane was prepared by means of a Grignard reaction, using diphenylgermanium dibromide and ethylmagnesium bromide.

2. Bromination of diphenyldiethylgermane was shown to yield diethylgermanium dibromide and phenyl bromide.

3. Triethylgermanium fluoride was brominated leading to the preparation of diethylgermanium oxide and diethylgermanium dibromide.

4. Diethylgermanium oxide was found to exist in two polymeric forms.

5. The ammonolysis of diethylgermanium dibromide was studied and diethylgermanium imine isolated.

PROVIDENCE, RHODE ISLAND

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

# THE VARIATIONS IN THE BEHAVIOR OF PHENYLETHENES AND ETHANES DURING CATALYTIC HYDROGENATION

BY WALTER H. ZARTMAN AND HOMER ADKINS

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A study of the effect of carbon containing substituents upon the ease of hydrogenation over nickel[1] has been continued by hydrogenating the series of compounds, phenylethylene (styrene), 1,2-diphenylethylene (stilbene), 1,1,2-triphenylethylene, 1,1,2,2-tetraphenylethylene, and 1,1-diphenyl-2-phenoxyethylene. These five compounds offer the opportunity of determining the effect of the phenyl group upon the hydrogenation of alkene linkages. The ethylenes are thereby converted into the corresponding ethane derivatives, which in turn offer the possibility of noting the effect of the presence of phenyl (and cyclohexyl) groups upon the hydrogenation of other phenyl groups. Pentaphenylethane and triphenylacetophenone were added to the group because it became apparent that a third effect of structure was manifesting itself, *i. e.*, the weakening of carbon to carbon linkages.

**Phenyl Groups and the Hydrogenation of Ethenes.**—There is presented in the first half of Table I a summary of certain data obtained in the hydrogenation of various phenyl substituted ethylenes. It is impractical to make an *exact* comparison of the effect of phenyl groups upon the hydrogenation of ethene linkages because there appears to be no set of conditions under which these five ethenes will undergo hydrogenation at a measurable rate. The pressure of hydrogen as well as the temperature has a marked effect upon the rate of these hydrogenations of ethene linkages. For example, 1,2-diphenylethylene at 20° required fifteen minutes at 93 atm., thirty-five minutes at 30 atm. and eighty minutes at 2.7 atm.

Phenylethylene was so readily hydrogenated over nickel that it was completely converted into ethylbenzene at 20° and 2.5 atm. pressure. The substitution of a second phenyl group in ethylene lowered the reactivity of the double bond but slightly toward hydrogenation. The substitution of a third phenyl group increased by ten-fold the time required at 20° for its hydrogenation as compared with diphenylethylene. Tetraphenylethylene was sufficiently resistant to hydrogenation so that the reaction did not occur at a measurable rate at 20° over nickel, and required over two hours at 100° under 125 atm. pressure. 1,1-Diphenyl-2-phenoxyethlyene was hydrogenated much more rapidly than was triphenylethylene but much less rapidly than was diphenylethylene.

The ethene linkage in four of the phenylethylenes was also hydrogenated

[1] Adkins, Zartman and Cramer, THIS JOURNAL, **53**, 1425 (1931).

TABLE I

HYDROGENATION OF PHENYL ETHENES AND ETHANES

| Hydrogen acceptor | Millimoles | Time, min. | Temp., °C. | Press., atm. | Catalyst, g. | Solvent, ml. | Product(s)[a] |
|---|---|---|---|---|---|---|---|
| **Ethylene Linkages** | | | | | | | |
| Phenylethylene (styrene) | 200 | 75 | 20 | 2.5±0.5 | 2 (Ni) | None | Ethylbenzene |
| Phenylethylene | 200 | 25 | 20 | 34±6 | 2 (Ni) | None | Ethylbenzene |
| Phenylethylene | 200 | 7 | 125 | 125±11 | 1 (Cu-Cr) | None | Ethylbenzene |
| 1,2-Diphenylethylene (stilbene) | 100 | 80 | 20 | 2.7±0.3 | 2 (Ni) | 75[b] | 1,2-Diphenylethane |
| 1,2-Diphenylethylene | 100 | 35 | 20 | 30±3 | 2 (Ni) | 75[b] | 1,2-Diphenylethane |
| 1,2-Diphenylethylene | 100 | 15 | 20 | 93±6 | 2 (Ni) | 75[b] | 1,2-Diphenylethane |
| 1,2-Diphenylethylene | 100 | 4 | 150 | 130±6 | 1 (Cu-Cr) | 75[b] | 1,2-Diphenylethane |
| 1,1,2-Triphenylethylene | 100 | 150 | 20 | 95±5 | 2 (Ni) | 75[b] | 1,1,2-Triphenylethane |
| 1,1,2-Triphenylethylene | 100 | 5 | 150 | 135±3 | 1 (Cu-Cr) | 75[b] | 1,1,2-Triphenylethane |
| 1,1,2,2-Tetraphenylethylene | 36 | 130 | 100 | 125±3 | 2 (Ni) | 75[b] | 1,1,2,2-Tetraphenylethane |
| 1,1,2,2-Tetraphenylethylene | 36 | 15 | 150 | 133±4 | 1 (Cu-Cr) | 75[b] | 1,1,2,2-Tetraphenylethane |
| 1,1-Diphenyl-2-phenoxyethylene | 100 | 80 | 100 | 110±10 | 2 (Ni) | 75[b] | 1,1-Diphenyl-2-phenoxyethane |
| **Phenyl Groups** | | | | | | | |
| Phenylethylene[d] | 200 | 100[c] | 125 | 113±10 | 2 (Ni) | None | Cyclohexylethane |
| 1,2-Diphenylethylene[d] | 100 | 185[c] | 120 | 103±16 | 2 (Ni) | 75[b] | 1,2-Dicyclohexylethane |
| 1,2-Diphenylethane | 55 | 35[c] | 175 | 120±7 | 2 (Ni) | 50[b] | 1,2-Dicyclohexylethane |
| 1,1-Diphenylethane | 55 | 105[c] | 175 | 125±3 | 2 (Ni) | 75[b] | 1,1-Dicyclohexylethane |
| 1,1,2-Triphenylethylene[d] | 100 | 225[c] | 160 | 110±16 | 2 (Ni) | 75[b] | 1,1,2-Tricyclohexylethane |
| 1,1,2,2-Tetraphenylethylene[d] | 50 | 130[c] 300 | 175 | 113±20 | 4 (Ni) | 75[b] | 1,1,2,2-Tetracyclohexylethane |
| 1,1,1,2-Tetraphenylethane | 40 | 125[c] 240 | 175 | 116±16 | 2 (Ni) | 75[b] | 1,1,1,2-Tetracyclohexylethane |
| 1,1-Diphenyl-2-phenoxyethylene[d] | 100 | 300[c] 330 | 160 | 107±11 | 2 (Ni) | 75[b] | Cyclohexyl-2,2-dicyclohexylethyl ether |
| Pentaphenylethane | 37 | 270[c] 390 | 125 | 115±17 | 4 (Ni) | 75[b] | Pentacyclohexylethane (6%)<br>Tricyclohexylmethane (77%)<br>Dicyclohexylmethane (58%) |
| Pentaphenylethane | 37 | 150[c] 200 | 160 | 115±15 | 2 (Ni) | 75[b] | Pentacyclohexylethane (20%)<br>Tricyclohexylmethane (42%)<br>Dicyclohexylmethane (45%) |

[a] All yields were practically quantitative except from pentaphenylethane. [b] Methylcyclohexane. [c] Time for hydrogenation of "middle 80%," *i. e.*, disregarding the time for the first and last 10%. The greater significance of these figures as compared with the time for complete hydrogenation has been previously discussed.[4] [d] The alkene linkage is so rapidly hydrogenated in this compound, under the conditions of the hydrogenation, that it was accomplished long before the temperature for the hydrogenation of the phenyl groups was reached.

over a copper–chromium oxide catalyst at 150°. This catalyst is not active for hydrogenation at temperatures as low as nickel. However, it is very active from 125–150° so that the hydrogenation of all four of the phenylethylenes went to completion within a few minutes at 150°.

The activity of the copper–chromium oxide catalyst in hydrogenating alkene linkages as first noted by Connor[2] and further illustrated above seems significant in connection with Lazier's hypothesis that oxides do not catalyze the hydrogenation of carbon to carbon double bonds.[3]

**Effect of Phenyl Groups upon the Hydrogenation of Phenyl Groups.**—A precise comparison of the rate of hydrogenation of the six phenylethanes under consideration would be very difficult of attainment. The difference in ease of hydrogenation makes it questionable whether all of them could be hydrogenated at a measurable rate at the same temperature. Even if this were possible there appears to be no ratio of catalyst to hydrogen acceptor which would enable a fair comparison to be made. This is true because there is such a large difference in the amount of hydrogen absorbed per mole of the various phenylethanes. The hydrogenation of ethylbenzene requires 3 moles of hydrogen while pentaphenylethane requires 15 moles of hydrogen. This would necessitate a choice being made between keeping the ratio of catalyst constant with respect, (1) to weight of hydrogen acceptor, or (2) to moles of hydrogen acceptor, or (3) to moles of hydrogen to be absorbed. One of these choices would be as open to criticism as another. A further complication enters in that the effect of any slow deactivation of the catalyst by heat or by the presence of accidental impurities is greatly magnified in the slower hydrogenations. Thus the slow hydrogenations become many times slower, while the more rapid hydrogenations are little, if any, affected by deactivation of the catalyst.

Thus it is impossible to draw any conclusions of a quantitative nature from the data in Table I on the hydrogenation of various phenylethanes to cyclohexylethanes. However, the following rather important conclusion appears to be justified. Although there is somewhat of a decrease in the rate of hydrogenation of phenyl groups as the number of these groups in the molecule increases, it will be seen that this decrease in rate is small when the great increase in molecular weight, number of unsaturated linkages, and complexity of the molecule is taken into consideration. This conclusion is also in accord with the finding that triphenylbenzene was hydrogenated without difficulty to tricyclohexylcyclohexane.[1] It thus appears that increase in the *number* of phenyl groups in a molecule does not inhibit or greatly slow down its rate of hydrogenation.

**Effect of Phenyl Groups upon the Cleavage of Carbon to Carbon Bonds.**—The hydrogenation over nickel of the ethanes containing four

[2] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

[3] Vaughen and Lazier, *ibid.*, **53**, 3719 (1931).

or less phenyl groups in the molecule proceeded smoothly and quantitatively to the corresponding cyclohexylethanes at temperatures from 120 to 175°. A very different result was obtained when pentaphenylethane was subjected to hydrogenation over nickel. In the case of this compound, even at 125°, the molecule was rapidly cleaved so that the major products were di- and tricyclohexylmethanes. A 20% yield of pentacyclohexylethane was obtained by a more rapid hydrogenation at 160°.

The further study (data in Table II) of the cleavage of carbon to carbon linkages by hydrogenation was carried out chiefly by using a copper–chromium oxide catalyst rather than nickel. This was advantageous, because while copper–chromium oxide catalyzes the cleavage it does not induce the hydrogenation of phenyl groups, so that the cleavage of the phenylethanes may be distinguished from a possible cleavage of cyclohexylethanes. Thus pentaphenylethane over the copper catalyst at 200° gave di- and triphenylmethane rather than the cyclohexylmethanes obtained with nickel. With this catalyst at 200° tetraphenylethane was also cleaved to diphenylmethane, and even triphenylethane showed a detectable amount of cleavage. However, diphenylethane appears to be quite resistant to cleavage. An oxygen substituted phenylethane (triphenylacetophenone) was also cleaved. The oxygen to carbon linkage in diphenylphenoxyethylene was also cleaved, the products being phenol and diphenylethane.

TABLE II

CLEAVAGE WITH COPPER–CHROMIUM OXIDE CATALYST[a]

| Hydrogen acceptor | Millimoles | Time, hrs. | Catalyst, g. | Solvent, ml.[b] | Product(s) |
|---|---|---|---|---|---|
| Triphenylacetophenone (β-benzopinacol) | 55 | 10 | 2 | 50 | 81% Triphenylmethane |
| Triphenylacetophenone | 50 | 8 | 2 | 100 | 22% Toluene<br>65% Triphenylmethane<br>12% Tetraphenylethylene |
| 1,1,2,2-Tetraphenylethylene | 24 | 6.5 | 2 | 50 | 90% Diphenylmethane |
| 1,1-Diphenyl-2-phenoxyethylene | 100 | 7.5 | 2 | 75 | 75% Phenol<br>67% 1,1-Diphenylethane |
| 1,1,1,2-Tetraphenylethane | 9 | 12 | 1 | 25 | 70% Toluene<br>85% Triphenylmethane |
| Pentaphenylethane | 20 | 12 | 1 | 25 | 60% Diphenylmethane<br>80% Triphenylmethane |
| 1,1,2-Triphenylethylene | 10 | 12 | 1 | 25 | 5% Diphenylmethane<br>70% 1,1,2-Triphenylethylene |
| 1,1,2,2-Tetracyclohexylethane | 10 | 12 | 2 | 25 | No reaction |
| 1,1,1,2-Tetracyclohexylethane | 13 | 12 | 2 | 25 | No reaction |
| Pentacyclohexylethane | 7 | 12 | 1 | 25 | No reaction[c] |

[a] 200° and 130 atm. pressure of hydrogen. [b] Methylcyclohexane is the solvent referred to except in the second experiment where ether was used. [c] There was also no cleavage in nine hours at 200°, 0.5 g. nickel catalyst with 2.7 millimoles of the ethane.

In contrast with the above is the finding that the cyclohexylethanes, even pentacyclohexylethane, resisted cleavage even after twelve hours at 200° in the presence of an active nickel or copper–chromium oxide catalyst.

## TABLE III

### ANALYSES AND PHYSICAL CONSTANTS

| Compound | Molecular formula or physical constants | M. p. or b. p. °C. obs. | Mm. | Analyses, % Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|
| Ethylcyclohexane | B. p.[d] 128–130° | B 128–130 | 738 | | | | |
| 1,2-Diphenylethane | M. p.[a] 51–52° | M 52–53 | | | | | |
| 1,2-Dicyclohexylethane | B. p.[a] 270–271°; [b] 274–275°; [c] 147–148.5° (12 mm.) | B 266–268 | 748 | | | | |
| 1,1,2-Triphenylethane | M. p.[e] 54–55°; [f] 53.5–54.5°; [h] 54° | M 54–55 B 209–211 | 12 | | | | |
| 1,1,2-Tricyclohexylethane[i] | $C_{20}H_{36}$ | B 191–192 | 8 | 86.86 | 86.80 86.94 | 13.14 | 13.37 13.28 |
| 1,1,2,2-Tetraphenylethane | M. p.[f] 209° | M 208–209 | | | | | |
| 1,1,2,2-Tetracyclohexylethane | $C_{26}H_{22}$ | M 158–159 | | 87.06 | 87.04 87.06 | 12.94 | 12.98 13.15 |
| 1,1,1,2-Tetracyclohexylethane[j] | $C_{26}H_{46}$ | M 112–114 | | 87.06 | 87.07 86.96 | 12.94 | 12.66 12.46 |
| 1,1-Diphenylethane | B. p.[a] 270–272°; [c] 143° (15 mm.); [h] 268–270° | B 130–133 | 10 | | | | |
| 1,1-Diphenyl-2-phenoxyethane | $C_{20}H_{18}O$ | M 64–65 B 214–217 | 8 | 87.54 | 87.24 87.54 | 6.62 | 6.79 6.82 |
| Cyclohexyl 2,2-dicyclohexylethyl ether[k] | $C_{20}H_{36}O$ | B 200.5–201 | 10 | 82.11 | 82.09 82.09 | 12.42 | 12.32 12.56 |
| 1,1-Dicyclohexylethane | B. p. [a] 256–257°; [c] 112° (7 mm.) | B 264–265 | 740 | | | | |
| Tetraphenylethylene | M. p. [f,g] 221° | M 221–222 | | | | | |
| Pentacyclohexylethane[l] | $C_{32}H_{56}$ | M 191–192 | | 87.18 | 86.97 86.72 | 12.82 | 12.90 12.96 |
| 1,1-Diphenyl-2-phenoxyethylene | $C_{20}H_{16}O$ | M 58–59 B 235 | 23 | 88.19 | 88.05 87.82 | 5.93 | 6.00 5.88 |

[a] Sabatier and Murat, *Compt. rend.*, **154**, 1771 (1923). [b] Ipatiev, *Ber.*, **40**, 1281 (1907). [c] Adams and Marshall, THIS JOURNAL, **50**, 1970 (1928). [d] Sabatier and Senderens, *Compt. rend.*, **132**, 1255 (1901). [e] Boeseken and Bastet, *Rec. trav. chim.*, **32**, 184 (1913). [f] Biltz, *Ann.*, **296**, 221 (1897). [g] Lévy and Lagrave, *Bull. soc. chim.*, **43**, 437 (1928). [h] Klages and Heilmann, *Ber.*, **37**, 1455 (1904). [i] $d_{25}^{25}$ 0.9301; $n_D^{25}$ 1.5030; $MR'_D$, calcd. 87.86; found, 87.81. [j] $d_{25}^{25}$ 0.9636; $n_D^{25}$ 1.5217; $MR'_D$, calcd. 113.38; found, 113.39. The compound solidified after several weeks. [k] $d_{25}^{25}$ 0.9495; $n_D^{25}$ 1.4947; $MR'_D$, calcd. 89.54; found, 89.69. [l] The di- and tricyclohexylmethanes had the properties previously noted.[1]

It thus appears that the successive substitution of phenyl groups in ethane lowers the binding power of the carbon to carbon linkage of ethane so that with five phenyl substituents the linkage may be broken at 125° with nickel as a catalyst. With a copper–chromium oxide catalyst the linkage may be broken at 200° when there are only three phenyl substituents. Cyclohexyl groups showed no labilizing effect upon carbon to carbon linkages.

## Experimental Part

The preparation of the copper–chromium oxide[2] and the nickel[4] ("sodium bicarbonate type A") catalysts have been described previously. Processes described in the literature were used for the preparation of phenylethylene (styrene) (b. p. 44–46° (40 mm.));[5] 1,2-diphenylethylene (m. p. 121–123°);[6] 1,1,2-triphenylethylene (m. p. 67–68°);[7] triphenylacetophenone (m. p. 168—170°);[8] 1,1,1,2-tetraphenylethane (m. p. 142–143°)[9] pentaphenylethane (softened at 161–162°)[9] and tetraphenylethylene (m. p. 220–222°);[10] except that in the case of the last compound dehydration was accomplished with sulfuric acid rather than with acetyl chloride. The monophenyl ether of unsymmetrical diphenylethyleneglycol ($(C_6H_5)_2C(OH)CH_2OC_6H_5$) was prepared as by Stoermer,[11] and converted into 1,1-diphenyl-2-phenoxyethylene in a 98% yield by refluxing it for twenty hours with 500 ml. of methanol containing 10 ml. of concentrated sulfuric acid. The resulting oil was taken up with carbon tetrachloride, distilled under reduced pressure, and crystallized from 95% alcohol or acetic acid and water. The data on the physical constants and analysis of this and other important compounds encountered in this investigation are given in Table III.

The experimental methods and apparatus were essentially the same as those previously described.[12] The products were separated by fractionation through Widmer columns of suitable size. The solvents used for the recrystallizations of three of the new compounds are as follows: 1,1,1,2-tetracyclohexylethane from ethyl acetate, 1,1,2,2-tetracyclohexylethane from benzene or methylcyclohexane, and pentacyclohexylethane from ethyl acetate.

## Summary

An increase in the number of phenyl groups in the phenylethenes increases the temperature and (or) pressure required for hydrogenation to the corresponding phenyl and cyclohexylethanes, and decreases the rate of hydrogenation under comparable conditions. However, the increase in difficulty of hydrogenation with increase in molecular weight is not large since tetraphenylethylene could be converted into the ethane at 100° and pentaphenylethane into pentacyclohexylethane at 125° at reasonably rapid rates.

[4] Adkins and Covert, *J. Phys. Chem.*, **35**, 1684 (1931).
[5] "Organic Syntheses," John Wiley and Sons, New York, 1928, Vol. VIII, p. 84.
[6] Hell, *Ber.*, **37**, 453 (1904).
[7] Hell and Wiegandt, *ibid.*, **37**, 1429 (1904).
[8] Paal, *ibid.*, **17**, 911 (1884).
[9] Gomberg and Cone, *ibid.*, **39**, 1461 (1906).
[10] Lévy and Lagrave, *Bull. soc. chim.*, **43**, 437 (1928).
[11] Stoermer, *Ber.*, **39**, 2288 (1906).
[12] Adkins and Cramer, THIS JOURNAL, **52**, 4349 (1930).

The successive substitution of phenyl groups in ethane materially lowers the stability of the linkage of the ethane carbon atoms so that when three phenyl groups are in the molecule the ethane may be cleaved at 200° over a copper–chromium oxide catalyst. Pentaphenylethane may be cleaved over nickel at temperatures as low as 125°. The labilizing effect (if any) of cyclohexyl groups on the ethane carbon atoms is so small that pentacyclohexylethane was perfectly stable at 200° over nickel or copper–chromium oxide catalysts.

Four cyclohexylethanes and three ethers have been prepared and described for the first time. Further evidence of the activity of the copper–chromium oxide catalyst for the hydrogenation of alkene linkages has been presented.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY]

# THE PREPARATION AND PROPERTIES OF A DOUBLE SERIES OF ALIPHATIC MERCAPTANS[1,2,3]

BY L. M. ELLIS, JR.,[4] AND E. EMMET REID[5]

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Though aliphatic mercaptans have been known for nearly a century, our knowledge concerning any of them except a few of the lower ones is not extensive. The purpose of the present investigation was to prepare the normal and alpha secondary mercaptans up to nonyl in high purity for accurate determinations of their physical properties and to provide materials for studies of their reactions, some of which have been published. It seemed desirable to have these series complete for the comparisons of properties within the series and with the corresponding series of alcohols.

The literature on the mercaptans through butyl is too extensive to quote. *n*-Amyl mercaptan was prepared by Pexters,[6] *n*-hexyl by Pelouze and

[1] This paper contains some results obtained in an investigation on "The Reactions of Certain Selected Organic Sulfur Compounds" listed as Project No. 28 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] A portion of the material in this paper is abstracted from a Dissertation presented by L. M. Ellis, Jr., to the Faculty of Philosophy of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1929.

[3] Presented before the Organic Section at the Atlanta meeting of the American Chemical Society, April, 1930.

[4] American Petroleum Institute Research Fellow.

[5] Director, Project No. 28.

[6] Pexters, *Bull. sci. acad. roy. Belg.*, 801 (1906).

Cahours,[7] hexane-thiol-2 by Erlenmeyer and Wanklyn,[8] *n*-heptyl by Wissinger,[9] heptane-thiol-2 by Henry,[10] *n*-octyl by Kahn,[11] and octane-thiol-2 by Levene and Mikeska,[12] but none of these has been thoroughly studied.

## Discussion

For brevity, such details of the experimental work as quantities and yields, along with the values found for the various properties determined, have been arranged in tabular form, Tables I, II, III, IV and V being concerned with various properties, and VI, VII and VIII chiefly with preparation. Included in the former are the mean coefficients of thermal expansion as calculated from the density data, the molal heats of vaporization of the higher mercaptans as calculated from the boiling point data

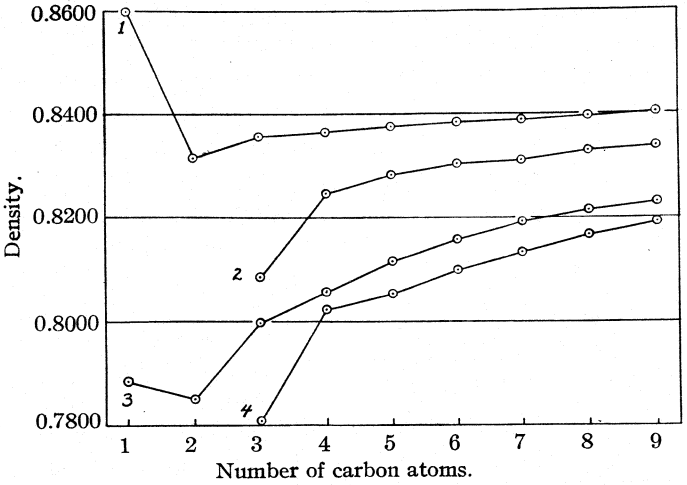


Fig. 1.—Densities of mercaptans and alcohols at 25°: 1, normal mercaptans; 2, α-secondary mercaptans; 3, normal alcohols; 4, α-secondary alcohols.

by use of the Clausius–Clapeyron equation, and the values for molecular refraction calculated by use of the Lorentz–Lorenz equation. For comparison with the last, values for molecular refraction as computed from atomic refraction data also are given, the two sets of values being headed respectively "found" and "calculated." Values for the atomic refraction of carbon, hydrogen, bromine and hydroxyl oxygen were taken from the

[7] Pelouze and Cahours, *Jahresber.*, 526 (1863).
[8] Erlenmeyer and Wanklyn, *Ann.*, **135**, 138 (1865).
[9] Wissinger, *Jahresber.*, 1280 (1887).
[10] Henry, *Rec. trav. chim.*, **28**, 444 (1909).
[11] Kahn, *Bull. soc. chem. Roumania*, **5**, 70 (1923).
[12] Levene and Mikeska, *J. Biol. Chem.*, **59**, 475 (1924).

work of Eisenlohr,[13] while that for the atomic refraction of sulfur was taken from the work of Price and Twiss.[14] Agreement between the "found" and "calculated" values is very close.

The values determined for the densities and refractive indices at 25° of the mercaptans and higher alcohols are illustrated by Figs. 1 and 3. To complete the curves, values from the work of Brunel[15] for the densities and refractive indices of the lower alcohols except the density of methyl alcohol, where the value given by Fischler[16] was used, are included in the plot. Resemblances between the curves for the corresponding mercaptans and alcohols are obvious. The point for the density of secondary heptyl mercaptan is apparently low. This may indicate the presence of a slight impurity, although none is shown by the analysis.

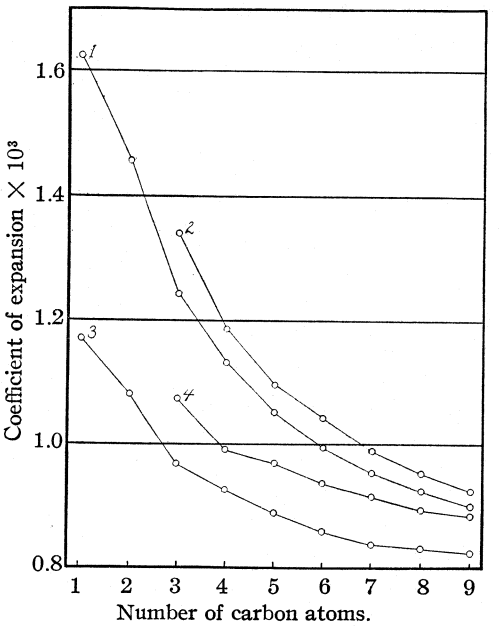


Fig. 2.—Mean coefficients of thermal expansion of mercaptans and alcohols from 0 to 25°: 1, normal mercaptans; 2, α-secondary mercaptans; 3, normal alcohols; 4, α-secondary alcohols.

Under the heading "expansion" in Tables I, II and V are given the mean coefficients of thermal expansion of the compounds over the range 0–25°. Figure 2 illustrates these for the mercaptans and alcohols. Here again there are obvious similarities between the curves for the corresponding alcohols and mercaptans. In order to obtain values for this property of the lower alcohols, densities obtained from the literature were plotted against temperature and the points for 0 and 25° read from the curves. In all cases only the values given by the same author for a compound were used in making these plots. Coefficients of expansion were calculated from the densities thus obtained using the values given for methyl alcohol by Klason and Norlin,[17] for ethyl alcohol by Winkler,[18] for propanol-1

[13] Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911).

[14] Price and Twiss, *J. Chem. Soc.*, **101**, 1263 (1912).

[15] Brunel, Crenshaw and Tobin, THIS JOURNAL, **43**, 574 (1921); Brunel, *ibid.*, **45**, 1338 (1923).

[16] Fischler, *Z. Electrochem.*, **19**, 128 (1913).

[17] Klason and Norlin, *Chem. Centr.*, II, 1480 (1906).

[18] Winkler, *Ber.*, **38**, 3614 (1905).

and propanol-2 by Atkins and Wallace,[19] and for butanol-2 by Timmermans and Martin.[20] All the values for the density of butanol-1 thus obtained from the literature resulted in a value for the coefficient of expansion badly off the curve, hence the density of a sample of boiling point 117.3 at 759 mm. was determined, the values being $d_4^0$ 0.82431; $d_4^{25}$ 0.80563. From these, the coefficient of expansion × 10 was calculated to be 0.9265.

TABLE I

PROPERTIES OF THE MERCAPTANS

Instead of giving the name of each compound in this and the subsequent tables the following system has been used: the Roman numeral gives the number of carbon atoms in the compound and the Arabic numeral indicates the number of the carbon atom to which the characteristic group is attached. Thus IV-1 designates normal butyl mercaptan, alcohol or bromide, according to the table heading, while IV-2 is butane-thiol-2, butanol-2 or 2-bromobutane.

| Mercaptan | Melting point, °C. | $d_4^0$ | $d_4^{25}$ | Expansion $1° \times 10^3$ | Latent heat of vaporization, g. cal. | $n_D^{25}$ | $MR_D$, found | $MR_D$, calcd. |
|---|---|---|---|---|---|---|---|---|
| I | −123.1 | 0.89482 | 0.85991 | 1.6239 | | | | |
| II | −147.3 | .86174 | .83147 | 1.4562 | | 1.4270 | 19.19 | 19.13 |
| III-1 | −113.3 | .86169 | .83572 | 1.2430 | | 1.4351 | 23.77 | 23.74 |
| III-2 | −130.7 | .83559 | .80851 | 1.3397 | | 1.4223 | 23.97 | 23.74 |
| IV-1 | −115.9 | .86006 | .83651 | 1.1261 | | 1.4401 | 28.41 | 28.36 |
| IV-2 | −165.0 | .84906 | .82459 | 1.1870 | | 1.4338 | 28.46 | 28.36 |
| V-1 | − 75.7 | .85952 | .83750 | 1.0517 | 8,847 | 1.4440 | 33.04 | 32.98 |
| V-2 | −169.0 | .85086 | .82815 | 1.0969 | 8,662 | 1.4386 | 33.06 | 32.98 |
| VI-1 | − 81.0 | .85911 | .83826 | 0.9949 | 9,836 | 1.4473 | 37.68 | 37.60 |
| VI-2 | −147.0 | .85217[a] | .83050 | 1.0437 | 9,146 | 1.4426 | 37.69 | 37.60 |
| VII-1 | − 43.4 | .85894 | .83891 | 0.9551 | 10,363 | 1.4498 | 42.33 | 42.22 |
| VII-2 | −141.0 | .85171 | .83114 | .9900 | 9,786 | 1.4452 | 42.35 | 42.22 |
| VIII-1 | − 49.2 | .85898 | .83956 | .9252 | 10,842 | 1.4519 | 46.97 | 46.83 |
| VIII-2 | − 79.0 | .85281 | .83293 | .9542 | 10,372 | 1.4481 | 47.00 | 46.83 |
| IX-1 | − 20.1 | .85907 | .84015 | .9008 | 11,522 | 1.4537 | 51.62 | 51.45 |
| IX-2 | − 69.0 | .85313 | .83384 | .9254 | 11,039 | 1.4500 | 51.64 | 51.45 |

[a] Erlenmeyer and Wanklyn[8] gave $d_0^0$ 0.8856, corresponding to $d_4^0$ 0.8854, for secondary hexyl mercaptan.

The melting points of the mercaptans given in Table I are illustrated by Fig. 4. These melting points were determined in this Laboratory by Dr. D. H. Andrews and Mr. Donald Teats, who have kindly permitted them to be included here. The normal mercaptans gave excellent melting points, but the secondary butyl, amyl, hexyl and heptyl compounds formed glasses, so that the melting points of these can be regarded only as approximate. For comparison, the melting points of the normal alcohols and hydrocarbons have been included in Fig. 4. In selecting values for these from the literature there was often considerable latitude of choice. The melting points used for methyl, ethyl and butyl alcohols were those

[19] Atkins and Wallace, *J. Chem. Soc.*, **103**, 1471 (1913).

[20] Timmermans and Martin, *J. chim. phys.*, **25**, 431 (1928).

TABLE II

PROPERTIES OF THE HIGHER ALCOHOLS

| Alcohol | $d_4^0$ | $d_4^{25}$ | Expansion per degree × $10^3$ | $n_D^{25}$ | $MR_D$, found | $MR_D$, calcd. |
|---|---|---|---|---|---|---|
| V-1 | 0.82963[a] | 0.811589[b] | 0.8896 | 1.4077 | 26.76 | 26.82 |
| V-2 | .82481[c] | .80528 | .9701 | 1.4041[c] | 26.76 | 26.82 |
| VI-1 | .83336[d] | .81581 | .8605 | 1.4161 | 31.42 | 31.43 |
| VI-2 | .82876[e] | .80977 | .9380 | 1.4126 | 31.42 | 31.43 |
| VII-1 | .83634[d] | .81915 | .8394 | 1.4222 | 36.04 | 36.05 |
| VII-2 | .83203 | .81340 | .9162 | 1.4190 | 36.05 | 36.05 |
| VIII-1 | .83848[d] | .82137 | .8332 | 1.4274 | 40.71 | 40.67 |
| VIII-2 | .83505 | .81678 | .8947 | 1.4244 | 40.69 | 40.67 |
| IX-1 | .84002[f] | .82303 | .8257 | 1.4320 | 45.43 | 45.29 |
| IX-2 | .83723 | .81910 | .8854 | 1.4290 | 45.37 | 45.29 |

[a] Lieben and Rossi[21] gave $d_0^0$ 0.8296, corresponding to $d_4^0$ 0.8294 for pentanol-1. [b] Holmes[22] gave $d_{25}^{25}$ 0.80915, corresponding to $d_4^{25}$ 0.80675, for pentanol-1. [c] Brunel[23] found $d_4^{25}$ 0.80483 and $n_D^{25}$ 1.4043 for pentanol-2. [d] Lieben and Janek[24] reported $d_0^0$ 0.8333, corresponding to $d_4^0$ 0.8331, for hexanol-1. [e] Zander[25] determined for this compound $d_0^0$ 0.8327, corresponding to $d_4^0$ 0.8325, $d_0^0$ 0.8342, corresponding to $d_4^0$ 0.8340, for heptanol-1, and $d_0^0$ 0.8361, corresponding to $d_4^0$ 0.8359 for octanol-1. For heptanol-1, Cross[26] reported $d_0^0$ 0.838, corresponding to $d_4^0$ 0.8379. [f] Zelinsky and Przewalsky[27] found $d_4^0$ 0.8287 for hexanol-2. Kraft[28] gave $d_4^0$ 0.8415 for nonanol-1.

given by Parks,[29] for propyl alcohol that given by Parks and Huffman,[30] for amyl alcohol by Simon,[31] for hexyl alcohol by Kelley,[32] for heptyl alcohol by Timmermans and Mattaar,[33] and for nonyl alcohol by "International Critical Tables." The melting point of octyl alcohol also was determined by Dr. Andrews and Mr. Teats. The melting point of methane was that given by "International Critical Tables." For ethane, propane and butane the melting points reported by Coffin and Maass[34] were used, for pentane that given by Timmerman,[35] for hexane and octane those given by Timmermans and Martin,[36] and for heptane and nonane the constants

[21] Lieben and Rossi, *Ann.*, **157,** 71 (1871).
[22] Holmes, *J. Chem. Soc.*, **103,** 2162 (1913).
[23] Brunel, THIS JOURNAL, **45,** 1334 (1923).
[24] Lieben and Janek, *Ann.*, **187,** 137 (1877).
[25] Zander, *ibid.*, **224,** 84 (1884).
[26] Cross, *ibid.*, **189,** 3 (1877).
[27] Zelinsky and Przewalsky, *Chem. Centr.*, II, 1185 (1908).
[28] Kraft, *Ber.*, **19,** 2221 (1886).
[29] Parks, THIS JOURNAL, **47,** 342 (1925).
[30] Parks and Huffman, *ibid.*, **48,** 2788 (1926).
[31] Simon, *Bull. soc. chim. Belg.*, **38,** 47 (1929).
[32] Kelley, THIS JOURNAL, **51,** 783 (1929).
[33] Timmermans and Mattaar, *Bull. soc. chim. Belg.*, **31,** 389 (1922).
[34] Coffin and Maass, THIS JOURNAL, **50,** 1433 (1928).
[35] Timmermans, *Bull. soc. chim. Belg.*, **25,** 300 (1916).
[36] Timmermans and Martin, *J. chim. phys.*, **25,** 411 (1928).

given in recent work by Midgley, Henne and Shepard.[37] The melting points of the normal mercaptans furnish a striking case of alternation with the high points coming where the compounds have an odd number of carbon atoms, whereas these points occur in the alcohols and hydrocarbons having even numbers of carbon atoms.

TABLE III

BOILING POINTS (°C.) OF HIGHER MERCAPTANS UNDER VARIOUS PRESSURES

| Mercaptan | 30 mm. | 50 mm. | 70 mm. | 90 mm. | 110 mm. | 150 mm. | 300 mm. | 760 mm. |
|---|---|---|---|---|---|---|---|---|
| V-1 | | | 57.7 | | 68.7 | 76.7 | 95.9 | 126.5 |
| V-2 | | | | | 55.9 | 63.9 | 83.6 | 112.9 |
| VI-1 | | 72.4 | | 86.4 | | 99.7 | 120.1 | 151.5[a] |
| VI-2 | | 60.6 | | 74.2 | | 87.5 | 107.3 | 138.9[b] |
| VII-1 | 81.2 | | 101.2 | | | 121.6 | 142.9 | 176.2[c] |
| VII-2 | 69.6 | | 89.2 | | | 109.5 | 130.4 | 163.6[d] |
| VIII-1 | 99.8 | | 120.6 | | | 142.1 | 164.0 | 199.1[e] |
| VIII-2 | 88.9 | | 109.1 | | | 130.1 | 151.7 | 186.4 |
| IX-1 | 117.4 | | 138.7 | | | 160.8 | 184.1 | 220.2 |
| IX-2 | 106.8 | | 128.1 | | | 149.9 | 172.4 | 208.2 |

[a] Pelouze and Cahours[7] gave 145–148° at atmospheric pressure as the boiling point of *n*-hexyl mercaptan. [b] Erlenmeyer and Wanklyn[8] reported 142° for this boiling point. [c] Wissinger[9] described *n*-heptyl mercaptan as boiling at 174–175° at 760 mm. Adams, Bramlett and Tendick[38] obtained a small amount of this compound, b. p. 174–176°, by the action of ethylmagnesium bromide on *n*-heptyl thiocyanate. [d] Henry[10] found 164–165° at 765 mm. for the boiling point of this compound. [e] Kahn[11] gave 198–200° for the boiling point of his *n*-octyl mercaptan.

TABLE IV

BOILING POINTS OF HIGHER ALCOHOLS AT 760 MM.

| Alcohol | Boiling point, °C. | Alcohol | Boiling point, °C. |
|---|---|---|---|
| V-1 | 137.8 | VII-2 | 158.7 |
| V-2 | 119.5 | VIII-1 | 194.7 |
| VI-1 | 156.5 | VIII-2 | 179.0 |
| VI-2 | 139.8 | IX-1 | 213.5 |
| VII-1 | 176.3 | IX-2 | 198.3 |

In acquiring the technique of the Cottrell apparatus used in determining the boiling points of the higher mercaptans under various pressures, given in Table III, similar determinations of the boiling points of the higher alcohols were carried out. The values thus obtained for the atmospheric boiling points of these alcohols are given in Table IV, and plotted in Fig. 5 along with the corresponding values for the mercaptans and those for the lower alcohols as given by Brunel and his co-workers.[15] Figure 6, based on the data of Table III, shows the shape of the vapor pressure–

[37] Presented at the Cincinnati meeting of the American Chemical Society, September, 1930, under the title "The Preparation and Physical Properties of Pure Normal Paraffins."

[38] Adams, Bramlett and Tendick, THIS JOURNAL, **42**, 2369 (1920).

temperature curve for each of the higher mercaptans. In Fig. 5 it will be observed that while the lower alcohols boil much higher than the corresponding mercaptans, this is reversed higher in the series, and in Fig. 6 it will be observed that the curves for the secondary mercaptans show more resemblance to those for the next lower normal compounds than to the normal compounds containing the same number of carbon atoms. In their work on the association and molecular constitution of the isomeric octanols and of a number of mercaptans, Bingham and his coworkers[39] show that of these the iso (or secondary) compounds are less associated than the corresponding normal ones, and that the degree of association decreases with increasing molecular weight. It appears possible, then, to explain

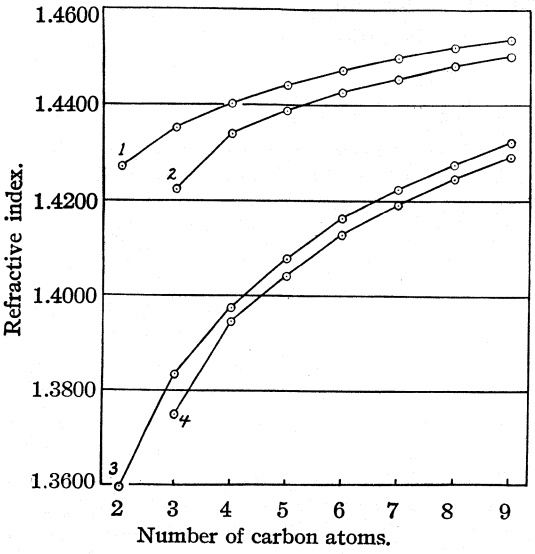


Fig. 3.—Refractive indices of alcohols and mercaptans at 25°: 1, normal mercaptans; 2, α-secondary mercaptans; 3, normal alcohols; 4, α-secondary alcohols.

TABLE V

PROPERTIES OF THE HIGHER BROMIDES

| Alcohol | $d_4^0$ | $d_4^{25}$ | Expansion per degree × $10^3$ | $n_D^{25}$ | $MR_D$, found | $MR_D$, calcd. |
|---|---|---|---|---|---|---|
| V-1 | 1.24313 | 1.21135 | 1.0494 | 1.4417 | 32.97 | 33.06 |
| V-2 | 1.23257[a] | 1.20056 | 1.0662 | 1.4394 | 33.12 | 33.06 |
| VI-1 | 1.19807[a] | 1.16899 | 0.9957 | 1.4452 | 33.59 | 37.67 |
| VI-2 | 1.18913 | 1.15979 | 1.0119 | 1.4432 | 37.74 | 37.67 |
| VII-1 | 1.16191 | 1.13484 | 0.9541 | 1.4480 | 42.24 | 42.39 |
| VII-2 | 1.14363 | 1.11634 | .9778 | 1.4450 | 42.70 | 42.39 |
| VIII-1 | 1.13337 | 1.10788 | .9203 | 1.4503 | 46.87 | 46.91 |
| VIII-2 | 1.12246 | 1.09681 | .9354 | 1.4482 | 47.15 | 46.91 |
| IX-1 | 1.10925 | 1.08490 | .8978 | 1.4523 | 51.53 | 51.63 |
| IX-2 | 1.10266 | 1.07806 | .9127 | 1.4507 | 51.69 | 51.63 |

[a] Karvonen[40] reported $d_4^0$ 1.2428 for normal amyl bromide, and $d_4^0$ 1.1992 for normal hexyl bromide. For the latter, Lieben and Janek[24] found $d_0^0$ 1.1935, corresponding to $d_4^0$ 1.1933.

[39] Bingham and Darrall, *J. Rheol.*, **1**, 174 (1930); Bingham and Fornwalt, *ibid.*, **1**, 372 (1930).

[40] Karvonen, *Chem. Centr.*, II, 1271 (1912).

the "crossing over" of the curves for the atmospheric boiling points by assuming a greatly decreased association in the higher alcohols, and to explain the appearance of the vapor pressure curves of the secondary mercaptans by the lesser association of these compounds as compared to the corresponding normal ones.

Figure 7, plotted from data kindly furnished the authors by Dr. E. C. Bingham of Lafayette College, illustrates the greater fluidity of the secondary as compared to the normal mercaptans, and the greater fluidity of the mercaptans as compared to the alcohols. Because the curve for the secondary alcohols fell so close to that for the primary compounds, values for the former were not included in this figure. A more complete discussion of these fluidities will be found in the previously mentioned work of Bingham.[39]

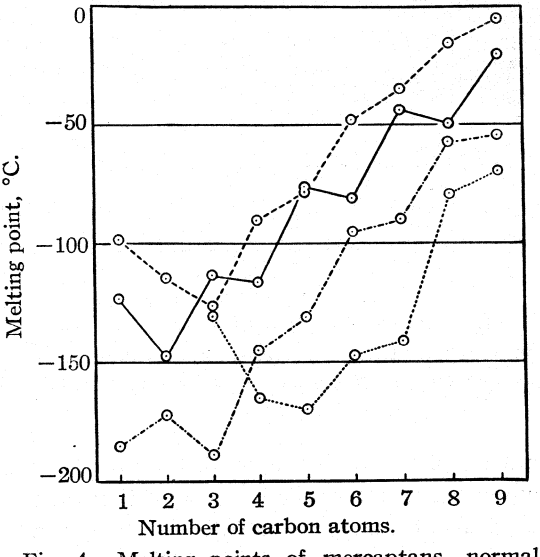


Fig. 4.—Melting points of mercaptans, normal alcohols and normal hydrocarbons: ————, normal mercaptans; .....,  α-secondary mercaptans; – – – –, normal alcohols; —·—·—, normal hydrocarbons.

In considering the yields of the mercaptans and bromides as given in Tables VI and VIII it must be remembered that purity of final product rather than high percentage yield was the desired object. In particular, the method of purification employed for the lower mercaptans resulted in heavy losses, while the close fractionation given the alkyl bromides caused low yields in several cases.

## Experimental Part

Fractionation of the intermediate bromides and of the samples of alcohols on which the physical constants were determined was accomplished by use of 112-cm. packed column stills of the general type described by Peters and Baker.[41] These stills had lagged columns and controlled reflux. A smaller still of the same type was used for fractionating the mercaptans. Except in the cases of methyl and ethyl mercaptans, density determinations were carried out by use of carefully calibrated pycnometers of about 8 cc.

[41] Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

volume, and were made either in duplicate or triplicate. The maximum deviation between any two accepted values on a compound was 0.00007.

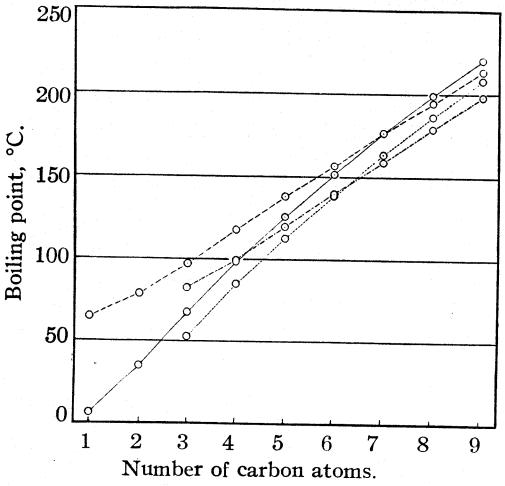


Fig. 5.—Atmospheric boiling points of alcohols and mercaptans: ——, normal mercaptans; - - - - -, α-secondary mercaptans; – – – –, normal alcohols; ·—·—·—, α-secondary alcohols.

The densities of methyl and ethyl mercaptans were determined by use of dilatometers of similar volume calibrated with distilled water and read with a cathetometer. Refractive indices were determined by use of an Abbé type refractometer with water-jacketed prisms maintained at 25° by circulating water from a thermostat. The boiling points of the higher mercaptans under various pressures were obtained by use of a Cottrell boiling point apparatus which required a sample of about 8 cc. Pressure control here and in the various vacuum distillations was accomplished by means of an apparatus to be described elsewhere. The temperature values given were determined by use of thermometers for which Reichsanstalt or Bureau of Standards certificates were available.

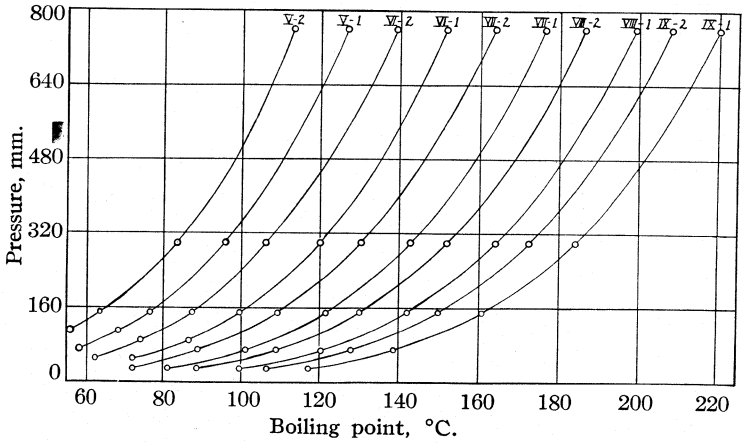


Fig. 6.—Boiling points of mercaptans under various pressures.

In the preparations, the alkyl bromide was prepared from the alcohol corresponding to the desired mercaptan, and the mercaptan prepared

in the usual manner by the action of an alkali hydrosulfide on the bromide. With the exception of heptanol-1, all the alcohols higher than butyl were made by the Grignard reaction. The preparation of the Grignard reagent and the addition of the various reactants, ethylene oxide, formaldehyde or other aldehydes, to this reagent was carried out in accordance with well-known procedure except in the preparation of octanol-1, where liquid formaldehyde was added to *n*-heptylmagnesium bromide in general accordance with a method developed by Glass and Reid.[42] Heptanol-1 was prepared by reducing heptaldehyde according to the method of "Organic Syntheses."[43] In order to obtain any reduction in this process it was found necessary to use degreased filings from cast iron instead of the grade specified. The alcohols were given a rough distillation and the major fraction boiling over a range of a few degrees collected. A portion of this crude product was then carefully distilled through one of the column stills to obtain the sample on which determinations of physical constants were carried out. The crude alcohol was then converted to the bromide, and this carefully fractionated in one of the column stills. Preparation of the two propyl, two butyl and *n*-amyl bromides was carried out according to the method of "Organic Syntheses,"[44] using portions of the corresponding commercial alcohols. The other alkyl bromides were prepared by a slight modification of that procedure. The alcohol was placed in a balloon flask equipped with a stirrer and reflux condenser, and for each mol of alcohol present 200 cc. of the more concentrated hydrobromic acid solution described in "Organic Syntheses" was added. The reaction mixture was stirred and heated in a water-bath kept at 80° if the alcohol was primary, or 60° if it was secondary. At the end of two hours another like portion of hydrobromic acid solution was added, and the treatment continued for another two hours. The stirring compensated for the slight solubility of the higher alcohols, while the relatively mild treatment prevented

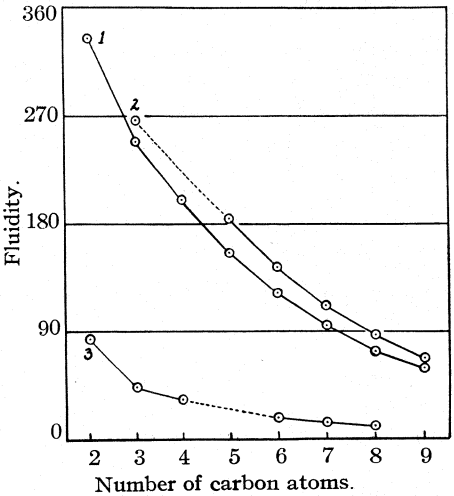


Fig. 7.—Fluidities of mercaptans and normal alcohols: 1, normal mercaptans; 2, α-secondary mercaptans; 3, normal alcohols.

[42] H. B. Glass, Dissertation, The Johns Hopkins University, 1929.

[43] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1926, Vol. VI, p. 62.

[44] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 5.

TABLE VI

PREPARATION OF MERCAPTANS AND MELTING POINTS OF ANTHRAQUINONE DERIVATIVES

| Mercaptan | Alkyl bromide used, g. | Mercaptan obtained, g. | Yield, % | Boiling range, °C. | Press., mm. | Purity titration | M. p. of anthraquinone thio ether, °C. |
|---|---|---|---|---|---|---|---|
| I | | | | 5.8– 6.2[b] | 756 | 100.1 | |
| II | | | | 34.4– 34.6[b] | 752 | 100.1 | |
| III-1 | 565 | 187 | 49.2 | 67.4– 67.6[c] | 763 | 99.5 | |
| III-2 | 565 | 140 | 36 | 52.3– 52.5[d] | 753 | 99.9 | |
| IV-1 | 685 | 241 | 53.5 | 98.6– 99.0[e] | 768 | 100.3 | |
| IV-2 | ... | ... | .. | 84.4– 84.6[f] | 754 | 99.7 | |
| V-1 | 302 | 145 | 69 | 126.3–126.5[g] | 759.5 | 99.9 | 128.8 |
| V-2 | 302 | 135 | 60 | 112.5–112.6 | 753 | 100.1 | |
| VI-1 | 330 | 158 | 67 | 86.0– 86.2 | 90 | 100.2 | 113.9 |
| VI-2 | 330 | 100 | 42 | 73.8– 74 | 90 | 99.8 | |
| VII-1 | 358 | 192 | 72 | 96.3– 96.5 | 59.5 | 100.2 | 95.9 |
| VII-2 | 358 | 102 | 38 | 85.0– 85.2 | 60 | 100.2 | |
| VIII-1 | 193 | 62 | 42.5 | 94.4– 94.6 | 25 | 99.6 | 95.2 |
| VIII-2 | 193 | 97 | 66 | 91.2– 91.5 | 35 | 99.9 | |
| IX-1 | 207 | 119 | 74 | 91.9– 92.4 | 10 | 99.7 | 117.5 |
| IX-2 | 207 | 118 | 73.7 | 89.7– 90 | 15 | 99.9 | |

[a] The anthraquinone derivatives of the lower mercaptans have been prepared by Reid, Mackall and Miller.[45] [b] Klason[46] gave 5.8° at 742 mm. as the boiling point of methyl mercaptan. Berthoud and Brun[47] reported it as 6.1–6.2° at 727 mm., and for ethyl mercaptan 33.4° at 724 mm. For the latter, Vespignani[48] and Ferretto[49] found 37° at 759.2 and 760.15 mm., and Naisini[50] gave 36.2–36.8° at 761 mm. [c] Roemer[51] records 67–68° as the boiling point of this compound. [d] Claus[52] reported 57–60° for this boiling point. [e] Saizew and Grabowsky[53] found 97–98° for the boiling point of *n*-butyl mercaptan. [f] Reymann[54] recorded 84–85° for the boiling point of secondary butyl mercaptan. [g] Pexters[55] gave 126° for the boiling point of *n*-amyl alcohol.[55]

charring or bad discoloration. The bromides were recovered by steam distillation, washed with water, with small portions of cold concentrated sulfuric acid, then with water and finally dried over anhydrous potassium carbonate.

Methyl mercaptan was prepared from dimethyl sulfate and potassium hydrosulfide according to the method of Klason.[56] Ethyl mercaptan was obtained from the Eastman Kodak Co. and purified as described below,

[45] Reid, Mackall and Miller, THIS JOURNAL, **43**, 1199 (1921).
[46] Klason, *Ber.*, **20**, 3049 (1887).
[47] Berthoud and Brun, *J. chim. phys.*, **21**, 159 (1924).
[48] Vespignani, *Gazz. chim. ital.*, **33**, I, 76 (1903).
[49] Ferretto, *ibid.*, **30**, I, 297 (1900).
[50] Naisini, *Ber.*, **15**, 2881 (1882).
[51] Roemer, *ibid.*, **6**, 784 (1873).
[52] Claus, *Ber.*, **5**, 659 (1872).
[53] Saizew and Grabowsky, *Ann.*, **171**, 251 (1874); **175**, 351 (1875).
[54] Reymann, *Ber.*, **7**, 1287 (1874).
[55] Pexters, *Bull. sci. acad. roy. Belg.* 801 (1906).
[56] Klason, *Ber.*, **20**, 3049 (1887).

TABLE VII

PREPARATION OF HIGHER ALCOHOLS[a]

| Alcohol | Prepared from | B. p. crude products, °C. | Pressure | Yield G. | Yield % | Final boiling range, °C. | Pressure, mm. |
|---|---|---|---|---|---|---|---|
| V-1 | $n$-$C_4H_9Br$ + HCHO | 132–142 | Atm. | 1910 | 56.4 | 137.5[b] | 754 |
| V-2 | $n$-$C_5H_7Br$ + $CH_3CHO$ | 118–119.5 | Atm. | 735 | 61.9 | 119.4[b] | 754 |
| VI-1 | $n$-$C_4H_9Br$ + $(CH_2)_2O$ | 152–158 | Atm. | 1109 | 40 | 100.5–101 | 90 |
| VI-2 | $n$-$C_4H_9Br$ + $CH_3CHO$ | 76– 79 | 65 mm. | 910 | 74.3 | 85.2– 85.5 | 90 |
| VII-1 | $n$-$C_7H_{14}O$ + H | 171–176 | Atm. | 3603 | 69.8 | 99.3– 99.5 | 40 |
| VII-2 | $n$-$C_5H_{11}Br$ + $CH_3CHO$ | 92– 97 | 70 mm. | 870 | 83.3 | 95.8– 96 | 70 |
| VIII-1 | $n$-$C_7H_{15}Br$ + HCHO | 110–117 | 50 mm. | 459 | 70.6 | 104.3–104.4 | 25 |
| VIII-2 | $CH_3I$ + $n$-$C_7H_{14}O$ | 102–105 | 52.5 mm. | 505 | 77.6 | 102.4–102.7 | 50 |
| IX-1 | $n$-$C_7H_{15}Br$ + $(CH_2)_2O$ | 98–102.5 | 10 mm. | 575 | 49.9 | 100.2–100.4 | 10 |
| IX-2 | $n$-$C_7H_{15}Br$ + $CH_3CHO$ | 100–103 | 12.5 mm. | 754 | 65.4 | 89.5– 89.8 | 10 |

[a] Commercial samples of the propyl and butyl alcohols were used after careful fractionation. [b] A number of boiling points are given in the literature for these compounds. The values given by "International Critical Tables" are 137.9° for normal, and 119.5° for secondary amyl alcohol. Such boiling points as are given in the literature for the other alcohols are at atmospheric pressure.

For the other mercaptans except secondary octyl and nonyl, 90 g. potassium hydroxide for each mol of bromide to be used was dissolved in alcohol (500 cc. 95% for the bromides below amyl, 400 cc., absolute for those above) and the solution saturated with hydrogen sulfide. This solution was then transferred to a flask of suitable size equipped with a reflux condenser and hydrogen sulfide inlet tube reaching nearly to the bottom of the flask. Hydrogen sulfide was passed slowly into the solution during all phases of the reaction to provide stirring and to keep the equilibrium as far as possible on the hydrosulfide side. The alkyl bromide was added slowly through the dropping funnel, after which the reaction mixture was allowed to stand for some time and heated either at 50–60° for two hours or at reflux for one hour. The reaction mixture was then diluted with a large volume of water and the mercaptan separated.

Among the impurities possibly present in mercaptans prepared in this manner are (1) unchanged bromide, (2) ethyl alcohol and (3) alkyl sulfide. Because of the wide divergence of their boiling points from those of the mercaptans, (3) and in the case of the higher mercaptans (2) would presumably be removed by distillation. The presence of (1) was suspected only in the cases of one or two of the lower mercaptans were the reaction did not appear to go to completion readily. The ethyl, the two propyl and the two butyl mercaptans were purified by dissolving them in 20% sodium hydroxide solution, extracting with a small portion of benzene, and steam distilling the alkaline solution until clear. Only a small amount of distillate had come over when this stage was reached. After cooling, the solution was faintly acidified with 15% sulfuric acid, and the mercaptan distilled out. The two amyl, two hexyl and two heptyl mercaptans were

TABLE VIII

PREPARATION OF ALKYL BROMIDES

| Bromide | Alcohol used, g. | Bromide obtained, g. | Yield, % | Boiling point, °C. | Pressure, mm. |
|---|---|---|---|---|---|
| III-1 | | | Approx. 50[a] | 70.7– 70.9[b] | 755 |
| III-2 | | | Approx. 40[a] | 59.4– 59.7[b] | 754 |
| IV-1 | | | Approx. 70[a] | 100.5–101.5[b] | 760 |
| IV-2 | | | Approx. 60[a] | 90.5– 91[b] | 756 |
| V-1 | 2040 | 1990 | 47.7 | 129.6–129.8[c] | 761 |
| V-2 | 645 | 760 | 67.6 | 118.6–118.9[d] | 761 |
| VI-1 | 992 | 867 | 54.1 | 87.8– 88 2 | 90 |
| VI-2 | 475 | 575 | 74.2 | 77.8– 78.1 | 90 |
| VII-1 | 3509 | 4485 | 82.8 | 94.0– 94.5 | 50 |
| VII-2 | 620 | 665 | 69.7 | 84.4– 84.6 | 50 |
| VIII-1 | 430[e] | 425 | 65.3 | 92.0– 92.5 | 10 |
| VIII-2 | 745[e] | 541 | 48.3 | 87.4– 87.9 | 25 |
| IX-1 | 490 | 410 | 58.2 | 94.3– 94.8 | 10 |
| IX-2 | 664 | 485 | 49.7 | 85.7– 86.2 | 10 |

[a] The propyl and butyl bromides were made in quantity for various preparations and no exact record of the yields was kept. [b] The boiling points given in "International Critical Tables" for the lower bromides are: *n*-propyl, 70.9°; isopropyl, 59.6°; *n*-butyl, 101.6°; *sec.*-butyl, 91.3°. The literature is too extensive to quote here. [c] The first portions of this bromide were distilled from 127.5–128.7° at 756 mm.; 1208 g. of this material was used in the preparation of heptanol-2. It was later found that a faint odor of formaldehyde in the bromide was removed by stirring for one hour with 5% sodium hydroxide solution. The balance of the bromide after this treatment gave the boiling point in the table. Although this is higher than the numerous values to be found in the literature, that given by "International Critical Tables" being 127.9°, it has been duplicated by other work[57] in this Laboratory. [d] Lucas, Simpson and Carter[58] reported 117–118° at 745 mm. as the boiling point of this bromide. [e] Portions of these alcohols were obtained from the Eastman Kodak Co.

similarly treated except that ether was substituted for the benzene, and the steam distillation omitted (the ease with which the mercaptans are distilled from alkaline solution increases with the molecular weight); the mercaptans were recovered by separating them from the acidified solution. No preliminary purification was given the other higher mercaptans; from the analyses, none was needed.

In the attempted preparation of secondary octyl and nonyl mercaptans by the previously outlined procedure, products were obtained which, from their boiling points, were almost entirely the sulfides. Rule[59] has shown that quite pure sodium hydrosulfide can be prepared by the action of hydrogen sulfide on sodium ethoxide, so the procedure for the preparation of these mercaptans was altered to take advantage of this. For each mol of the alkyl bromide to be used, 40 g. of sodium was dissolved in 500 cc. of ab-

[57] F. C. Wagner, Dissertation, The Johns Hopkins University, 1929.

[58] Lucas, Simpson and Carter, THIS JOURNAL, **47**, 1467 (1925).

[59] Rule, *J. Chem. Soc.*, **99**, 560 (1911).

solute ethyl alcohol, and this saturated with hydrogen sulfide. Since a large amount of the sodium hydrosulfide came out of the solution, mechanical stirring was used during the addition of the alkyl halide. The other procedure was as previously described.

Preparation of the anthraquinone $\alpha$-alkyl thio-ethers was carried out according to the method of Reid, Mackall and Miller,[60] except that the time of refluxing was doubled. The compounds were recrystallized from alcohol, benzene, methanol or mixtures of these. It was not found possible to obtain satisfactory melting points for the derivatives of the higher secondary mercaptans.

The mercaptans were analyzed for total hydrosulfide content by oxidation to the disulfide with excess standard iodine solution according to the method of Kimball, Kramer and Reid.[61] The results were calculated to percentage purity, the values given in Table VI representing the mean of several determinations. The widest deviation between any of the individual determinations on a mercaptan was approximately 1%.

The authors wish to express their thanks to Dr. R. F. Deese, Jr., whose assistance in this work included the determination of the densities of the higher bromides which are included in Table V.

## Summary

1. Normal and alpha secondary mercaptans from methyl through nonyl, and a number of intermediate alcohols and bromides, have been prepared. The mercaptans have been analyzed.

2. The densities at 0 and 25°, and the refractive indices at 25° have been determined for the mercaptans and the higher alcohols and bromides. The mean coefficients of thermal expansion over this range and the values for molecular refraction have been calculated for these compounds.

3. The melting points of the mercaptans have been given.

4. The boiling points at various pressures have been determined for the higher mercaptans.

5. The anthraquinone $\alpha$-alkyl thio-ethers have been prepared from the higher normal mercaptans and their melting points determined.

6. Curves illustrating certain relationships between these mercaptans and alcohols have been given.

BALTIMORE, MARYLAND

[60] Reid, Mackall and Miller, THIS JOURNAL, **43**, 2104 (1921).

[61] Kimball, Kramer and Reid, *ibid.*, **43**, 1199 (1921).

# COMMUNICATIONS TO THE EDITOR

## PHOTOSYNTHESIS IN VITRO

*Sir:*

Baly[1] originally required a pre-activated catalyst of colloidal nature for the reduction of carbon dioxide to formaldehyde and carbohydrates *in vitro*. Neither Emerson[2] nor Zscheile[3] confirms his results. Later, supporting his catalyst on an aluminated kieselguhr, Baly[4] found pre-activation unnecessary. Bell[5] does not confirm this. Baly[6] has insisted throughout that the catalyst must be alkali-free. Dhar, Rao and Ram,[7] and Rao and Dhar[8] obtain formaldehyde with nickel carbonate and colloidal ferric hydroxide as catalysts in alkaline solution (2% $NaHCO_3$).

In synthesizing formaldehyde there are two essentials: an active catalyst, and light of the proper wave length. Rao and Dhar (Ref. 8, p. 1424) used glass containers, stating that the ultraviolet under such conditions must be of limited effect. Kruyt and van der Spek[9] state that $Fe(OH)_3$ can be negatively charged in a limited range of alkaline concentrations. More alkali precipitates the sol, independently of the concentration of the catalyst. Pure $Fe(OH)_3$ sols appear unstable in 2% $NaHCO_3$. Rao and Dhar's $NiCO_3$ was apparently not colloidal.

The writer prepared catalysts as follows: (a) $Fe(OH_3)$—Krecke's method; (b) $NiCO_3$—(1) triturated $NiCO_3$ (Kahlbaum) washed free from chloride and sulfate with boiling water, (2) by precipitation from the nitrate with $NaHCO_3$, removing the nitrate by dialysis.

The following experiments were performed: (a) 500 cc. of 2% $NaHCO_3$ (Merck's c. p.) with $NiCO_3$ (quantities ranging from 0.2–10 g.); (b) 500 cc. of 2% $NaHCO_3$ with $Fe(OH)_3$ (approximately 0.5 g. added from a stable aqueous sol); (c) 500 cc. of 2% $NaHCO_3$ with $NiCO_3$, 1 g. and 25 cc. of 0.1% dimedone solution.

All were exposed for sixty hours to sunlight. The flasks were periodically shaken, as the catalyst settled out. Tests were made on all for formaldehyde (Schiff's reagent, described by Rao and Dhar) and for carbohydrates (Molisch's reagent). The sediment in experiment (c) was examined for the typical crystals that formaldehyde forms with dimedone. All results were negative.

[1] Baly, *Science*, **68**, 364–365 (1926).
[2] Emerson, *J. Gen. Physiol.*, **13**, 163 (1929).
[3] Zscheile, THIS JOURNAL, **54**, 973 (1932).
[4] Baly, *Nature*, **126**, 666 (1930).
[5] Bell, *Trans. Faraday Soc.*, **27**, 771 (1931).
[6] Baly, "Photochemical Processes," Faraday Soc. April, p. 545 (1931).
[7] Dhar, Rao and Ram, *ibid.*, p. 554.
[8] Rao and Dhar, *J. Phys. Chem.*, **35**, 1419–1432 (1931).
[9] Kruyt and van der Spek, *Kolloid-Z.*, **25**, 1–20 (1919).

Later, in a letter, Professor Dhar emphasized the necessity of incident light of wave lengths 2900–3000 Å. and preferred Schryver's test to Schiff's. The writer then irradiated an uncovered beaker containing 300 cc. of 2% $NaHCO_3$ and colloidal $Fe(OH)_3$ with a mercury arc lamp. Schryver's and Molisch's tests were negative.

The status of this problem is extraordinarily involved, though it can hardly be doubted that some workers have succeeded in obtaining formaldehyde *in vitro*. Baly[4] claims that small amounts of thorium oxide markedly affect yields. Accurate quantitative data are required, particularly with varying amounts of impurities which promote or inhibit the reaction. The writer cannot claim, either with sunlight or with the arc lamp, to have duplicated exactly the illumination used by Rao and Dhar. The Indian sunlight may be sufficiently intense in the ultraviolet region that glass containers do not filter out all these rays. With the arc lamp, secondary reactions may occur, *e. g.*, polymerization of formaldehyde to sugars, though the writer found none.

One concludes that no procedure has yet been published whereby conditions for obtaining formaldehyde and carbohydrates *in vitro* can be duplicated in other laboratories.

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RECEIVED FEBRUARY 3, 1932
PUBLISHED APRIL 6, 1932

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## GASEOUS PHOTO DECOMPOSITION OF CHLORINE DIOXIDE

*Sir:*

Qualitative investigations of the photo formation of $Cl_2O_6$ from $ClO_2$ have already been made.[1,2] Bodenstein and Schumacher[3] discuss this reaction and arrive at one molecule of $Cl_2O_6$ per two quanta absorbed, their equations leading to a maximum decrease in volume of one mole per einstein. The absorption spectrum of $ClO_2$[4] indicates a region of predissociation below 3750 Å. The schemes given by Schumacher for decomposition in this region and the Band region lead to the same decrease in volume per einstein as before.

Preliminary quantitative experiments on the gaseous photo $ClO_2$ decomposition point to a chain reaction. $ClO_2$ was prepared by the method used by Bodenstein[2] and no attempt was made to remove $Cl_2$. The gas was contained in a Suprax cell 10 cm. long, fitted with plane ends 5 cm. in diameter. The cell was filled by streaming a small percentage of the

[1] Booth and Bowen, *J. Chem. Soc.*, 510 (1925).
[2] Bodenstein, Harteck and Padelt, *Z. anorg. Chem.*, **147**, 233 (1925).
[3] Bodenstein and Schumacher, *Z. physik. Chem.*, **5B**, 233 (1929).
[4] Schumacher, *Z. physik. Chem.*, Bodenstein Band, 704 (1931).

gas through in the presence of oxygen, at a total pressure of one atmosphere and at 15°. The reaction was followed by the pressure changes on a sulfuric acid manometer.

The light absorbed was measured with a thermopile–galvanometer system which was calibrated using a filament lamp from the Bureau of Standards and checked by experiments on $Cl_2$–$O_3$ mixtures. On insolation with light of 3650 Å. there was a sharp decrease in pressure which was eventually followed by an almost equally sharp increase in pressure. The decrease in pressure in the first part of the experiment appears to be due to the formation of $Cl_2O_6$ and its deposition on the walls. It is suggested that the increase in pressure which follows is due to the sensitized decomposition of $Cl_2O_6$ by Cl atoms.[5] Using higher concentrations of $ClO_2$, larger amounts of $Cl_2O_6$ accumulate and after-effects of insolation indicate that it may start to decompose at an appreciable rate before all the $ClO_2$ has decomposed, and furthermore it does not all decompose to $Cl_2 + O_2$. One would expect the state of the surface to be an important factor.

The final rise in pressure shows a close resemblance to that obtained with $Cl_2$–$O_3$.[6] A similar rise is recorded in one experiment[7] with $Cl_2O$ and since the formation of $ClO_2$ has been shown to occur in this reaction it is possible that it can also be explained by the final decomposition of $Cl_2O_6$, which only occurs when Cl atoms are no longer used up by $ClO_2$, $Cl_2O$ and $O_3$ in the different experiments. Quantitative experiments with 3650 Å. showed an over-all decrease in volume varying between 5 and 23 moles per einstein in the first part of different experiments on the photo decomposition of gaseous $ClO_2$, while the end gave increases in volume up to 10 moles per einstein absorbed, indicating that we are probably dealing with a chain reaction.

[5] Allmand and Spinks, *Chem. News*, **142**, 333 (1931).
[6] Allmand and Spinks, *J. Chem. Soc.*, 1652 (1931).
[7] Finkelnburg, Schumacher and Stieger, *Z. physik. Chem.*, **15B**, 153 (1931).

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J. W. T. SPINKS

RECEIVED FEBRUARY 9, 1932
PUBLISHED APRIL 6, 1932

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## ALKYLATIONS OF NITRILES IN LIQUID AMMONIA

*Sir:*

The reaction of phenylacetonitrile which has been communicated by J. A. Nieuwland and L. H. Baldinger [THIS JOURNAL, **54**, 828 (1932)] has also been observed by the writer and E. C. Knowles [Knowles, M. S. Dissertation, R. P. I., 1929]. Similar alkylations of nitriles in liquid ammonia have also been reported [Cloke, Anderson, Lachmann and Smith, THIS JOURNAL, **53**, 2791 (1931); Knowles and Cloke, "Substituted Phenyl-

acetonitriles and Derivatives," in press]. These facts are mentioned since we are still at work on similar alkylations, which, however, are probably distinct from those under way at Notre Dame.

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RECEIVED FEBRUARY 13, 1932
PUBLISHED APRIL 6, 1932

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## ISOLATION OF SPARTEINE FROM LUPINUS BARBIGER (WATSON)

*Sir:*

Sparteine has been found in one species of lupine, *L. luteus*, where it is accompanied by a second alkaloid, lupinine. Although a number of other species of lupines has been examined these two alkaloids have not again been found. The isolation of sparteine from *L. barbiger*, recently effected in this Laboratory is, therefore, of interest.

Leaves and stems of this plant, collected at Hilltop, ten miles north of Fairview, Utah, were obtained through the courtesy of A. B. Clawson and were identified by W. W. Eggleston. The alkaloids were extracted[1] and submitted to the action of solvents to separate them. The fraction soluble in petroleum ether contained sparteine and a second base from which it could not be separated by fractional distillation in a vacuum. The mixture yielded a picrate, platinum chloride and methiodide which had the constants of sparteine. Separation was effected through the mercuric chloride double compound, from which pure sparteine could be recovered by treatment with ammonia, shaking out with chloroform, removing the solvent and distilling under reduced pressure. The greater part came over at 185° and 7 mm. and showed $n_D^{27}$ 1.5256 and $[\alpha]_D^{30}$ −6.07°. Willstätter and Marx[2] gave −5.96° at 20°. Moureu and Valeur[3] give $n_D^{19}$ 1.5293. The indices of refraction for a specimen of authentic sparteine were determined in this Laboratory as 1.5263 (24°), 1.5253 (26°), 1.5248 (28°), 1.5242 (29°). The specimen from *L. barbiger* was positive to the Jorissen[4] $H_2S$–S and the modified Grant[5] tests for sparteine. The picrate melted at 205–206° and did not depress the m. p. of sparteine picrate. The platinum chloride melted with decomposition at 248° and did not depress the melting point of sparteine platinum chloride.

The hydrobromide melted at 197° and was levorotatory $[\alpha]_D^{29}$ −18.33°. Found: $H_2O$, 4.40, 4.54; Br, 38.51, 38.50. $C_{15}H_{26}N_2 \cdot 2HBr \cdot H_2O$ requires

[1] The procedure was in general that already described, THIS JOURNAL, **47**, 2584 (1925).

[2] Willstätter and Marx, *Ber.*, **37**, 2351 (1904).

[3] *Bull. soc. chim. Paris*, [3] **29**, 1135 (1903).

[4] *Anal. Chim. Analyt.*, **16**, 412 (1911).

[5] *Am. J. Pharm.*, **97**, 38 (1925).

$H_2O$, 4.35; Br, 38.63. The alkaloid regenerated from a portion of the salt showed $n_D^{27}$ 1.5259 and yielded a picrate, m. p. 206°.

The methyl iodide was readily prepared by mixing the original fraction with excess of methyl iodide and allowing to stand in the cold. After a half-hour the whole solidified to a mass of white crystals. Sparteine usually shows no such behavior. A mixture of sparteine and methyl iodide remains liquid for weeks, unless warmed, but eventually deposits crystals. In our preparation the second alkaloid appears to catalyze the reaction.

The methyl iodide so prepared was recrystallized several times from alcohol. Dried in a desiccator the purest crop melted at 239–240°. Found: N, 7.51; I, 33.72, 33.63. $C_{15}H_{26}N_2CH_3I$ requires N, 7.45; I, 33.75. Moureu and Valeur[3] give the melting point "about 240°." Further crops of crystals obtained in the above preparation gave 6.91 and 7.19% N, indicating admixture with the second alkaloid.

These data establish the presence of sparteine in *L. barbiger*. Two or three other alkaloids are present but are not sufficiently characterized at present for identification. No evidence indicating the presence of lupinine has as yet been obtained.

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JAMES FITTON COUCH

RECEIVED FEBRUARY 29, 1932
PUBLISHED APRIL 6, 1932

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## OXIDATION OF THE ALPHA AND BETA FORMS OF THE SUGARS

*Sir:*

In the course of studies on the oxidation of the sugars with bromine water experimental conditions have been developed by means of which it is possible to follow the oxidation of a single form of a sugar. The crystalline sugar is added to a suspension of barium carbonate in bromine water saturated with carbon dioxide, and the reaction is allowed to continue while stirring the mixture and holding the temperature constant. At intervals samples of the solution are taken and the amount of oxidation is determined by analysis. Through the buffer action of the barium carbonate and carbon dioxide the solution is maintained in a slightly acid condition ($P_H$ 6). As a result the mutarotation of the sugar is relatively slow and the oxidation is relatively rapid. Equilibrium between the various forms of the sugar is not established prior to oxidation and consequently the reaction rates depend largely on the particular forms of the sugars used. There are marked differences in the rates obtained with various sugars and in the rates obtained with different forms of a given sugar.

Thus the oxidation of a sample of beta lactose is about 95% complete in three minutes, while under like conditions the reaction of alpha lactose is

only about 50% complete. This marked difference in the reaction rates affords a new method for ascertaining the approximate amounts of the alpha and beta isomers in solution. Such data should be of value in the study of the mechanism of the oxidation reactions and also for determining whether a given crystalline form of a sugar consists of a single isomer or whether it is a mixture of the alpha and beta forms. The oxidation of the sugar containing a single isomer progresses uniformly, while the oxidation of a mixture of the alpha and beta forms progresses rapidly until one form, usually the beta, is used up, and then more slowly as the oxidation of the other form is continued. Inasmuch as homogeneous crystalline compounds containing the alpha and beta forms of a single sugar have been discovered recently by Hockett and Hudson [THIS JOURNAL, **53**, 4455 (1931)] it is necessary to determine whether or not the known crystalline sugars are substances of this type. This problem may be attacked by determining the rates at which they are oxidized by bromine water.

Since a large number of the sugars are being studied under strictly comparable conditions, the results may be used also in correlating the rate of oxidation with the stereomeric structure of the sugars.

The writer is being assisted in this work by W. W. Pigman.

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RECEIVED MARCH 2, 1932
PUBLISHED APRIL 6, 1932

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## THE NATURE OF ACTIVATED ADSORPTION

*Sir:*

In a recently published article [THIS JOURNAL, **54**, 602 (1932)] Taylor and Sickman presented data on the low- and high-temperature adsorption of hydrogen by zinc oxide, from which some information on the two types of adsorption can be secured by statistical methods. From their Fig. 3 on page 612, it is found that equal amounts are adsorbed at 125°K. and 580°K. and 400 mm. pressure, while the heats of adsorption are 1100 and 21,000 cal., respectively. Writing statistical expressions for exp. $(-f/kt)$ ($f$: free energy at constant pressure in $\mu$ space), setting free energy of gas equal to that of adsorbate at each temperature and dividing the square of the expression for 125°K. by that for 580°K. the following equation results

$$e^{(2\Delta\epsilon_1/KT_1) - (\Delta\epsilon_2/KT_2)} = \frac{T_1^3 h^3}{T_2^{7/2} P 2^{5/2} \pi^{5/2} m^{1/2} k^{1/2} J} \frac{\Omega_{v_2}^6}{\Omega_{v_1}^2} \frac{N^2}{S^2}$$

The assumptions underlying this expression are that in low temperature adsorption hydrogen molecules have freedom of motion over the surface (two dimensional ideal gas) and that their rotation is unchanged by

adsorption, while at high temperature hydrogen atoms are produced which are held by definite surface atoms. Further, $m$ and $J$ are the mass and the moment of inertia of hydrogen molecules, $\Omega_{v_1}$ is the phase space of vibration (in $h$ units) normal to the surface in low temperature adsorption, $\Omega_{v_2}$ is the phase space of vibration of adsorbed atoms at higher temperature, $P$ is the gas pressure, $S$ is the surface available for the low temperature adsorption in sq. cm., while $N$ is the number of surface atoms available for the high temperature adsorption. Assuming, in the first approximation, that the zero point energy changes $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are equal to the measured heats of adsorption, the numerical calculation yields

$$\frac{N}{S} = 2 \times 10^{12} \frac{\Omega_{v_1}}{\Omega_{v_2}^3}$$

Since the ratio $\Omega_{v_1}/\Omega_{v_2}^3$ is hardly much larger than unity and the total number of surface atoms per sq. cm. is of the order of $10^{15}$, it is seen that only a small fraction of the surface participates in the "activated" adsorption. Other assumptions regarding the state of adsorbed gases lead to still smaller fractions of the surface involved in high temperature adsorption. Thus, if in activated adsorption hydrogen molecules retain their identity and execute a rotational motion in addition to vibration as a whole ($\Omega_{v_2}$) around their position of equilibrium, the expression is obtained

$$\frac{N}{S} = 2 \times 10^{11} \frac{\Omega_{v_1}}{\Omega_{v_2}^3}$$

If, finally, freedom of motion on the surface is accepted for activated adsorption, the ratio of surfaces involved in the two processes is found to be

$$\frac{S_2}{S_1} = 10^{-5} \frac{\Omega_{v_1}}{\Omega_{v_2}}$$

A larger fraction of surface involved in activated adsorption than calculated above, is obtained only if formation of multimolecular layers at low temperature is postulated. These calculations lead to the conclusion that activated adsorption is limited to particular surface atoms only, the adsorbate not forming a freely moving two-dimensional gas on the surface (*cf.* H. S. Taylor, "Catalytic Symposium," Faraday Society, 1931); they indicate at the same time a way for a detailed study of the structure of surfaces by measurements of heat changes in adsorption of varying amounts at low and high temperatures. It should be pointed out also that in calculations of the theoretical adsorption rate, correction must be made for the inactive surface.

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RECEIVED MARCH 4, 1932
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## THE SPECIFIC NATURE OF ENERGY EXCHANGE IN UNIMOLECULAR REACTIONS

*Sir:*

Since the energy of activation in unimolecular reactions is undoubtedly obtained by collision, the velocity constants fall off at low pressures. It is well known that certain inert gases will prevent this falling off by furnishing the necessary collisions. The specific nature of this effect is, however, very remarkable. In general, hydrogen and the products of the reaction are effective, while other inert gases are usually ineffective. Rice has recently discussed the question from the point of view of quantum mechanics [O. K. Rice, *Chem. Reviews*, **10,** 125 (1932)].

In the past most of the inert gases employed have been of comparatively simple structure. It seems desirable to obtain information regarding the behavior of gases which are as complicated as the reactant, and which resemble the reactant as much as possible. The series of ether decompositions investigated by Hinshelwood and his co-workers are ideal for the purpose. Accordingly an investigation has been undertaken on the rate of decomposition of mixtures of aliphatic ethers. Mixtures of dimethyl and diethyl ether have already been investigated. These ethers decompose in an almost identical way, and have a pronounced resemblance in physical properties, and in the manner in which the velocity constants fall off with diminishing pressure. Each might therefore be expected to show a high efficiency in activating the molecules of the other.

The surprising result has been obtained that the two gases have absolutely no activating effect on each other. A mixture of the two (at pressures where the falling-off is large) decomposes at a rate which is exactly the mean of those of its components (within an experimental error of about three per cent.). This appears to be the most pronounced example of the specificity of energy transfer which has yet been observed.

The decomposition of mixtures of methyl ethyl ether with both diethyl and dimethyl ether is being investigated. A full account of the work will appear later.

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RECEIVED MARCH 7, 1932
PUBLISHED APRIL 6, 1932

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## THE PREPARATION OF AN OPTICALLY ACTIVE TRIARYLCARBINOL

*Sir:*

A survey of the chemical literature shows that many primary and secondary alcohols containing an asymmetric carbon atom have been successfully resolved. However, all previous attempts to resolve asymmetrically substituted tertiary alcohols have failed. In an 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, $(C_6H_5)(C_6H_5C_6H_4)(C_{10}H_7)CSCH_2COOH$, was prepared and resolved by means of its brucine salt. It was found to have the specific rotation in carbon tetrachloride, $[\alpha]_D^{20}$ −13.63°; in ether, $[\alpha]_D^{20}$ −12.93°. The dextro modification obtained by working up the residues from the fractional crystallization of the brucine salt gave an acid with $[\alpha]_D^{20}$ +10.6° in ether.

Many experiments have been carried out on these compounds in order to convert them into the corresponding optically active triarylcarbinols. This has finally been accomplished. Under proper conditions the levo modification of the acid gives a *d*-phenylbiphenyl-α-naphthylcarbinol of the specific rotation in carbon tetrachloride, $[\alpha]_D^{20}$ +5.8°. The dextro modification of the acid yields a levorotatory-carbinol, $[\alpha]_D^{20}$ −5.4°. The corresponding ethyl ethers have been prepared. The levo acid produces a levorotatory ether, $(C_6H_5)(C_6H_5C_6H_4)(C_{10}H_7)C{-}OC_2H_5$, $[\alpha]_D^{20}$ −22.7° in ether. The dextro acid gives a dextrorotatory ether, $[\alpha]_D^{20}$ +21.6°. Other asymmetrically substituted tertiary alcohols are being prepared in order to study their possibilities of resolution by this method. Further investigations on the above optically active compounds are in progress with a view of answering the question of the spatial arrangement of the valences of the trivalent carbon atom. At present this is completely unexplained, and has been but superficially investigated. A report of this work will be published later.

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EVERETT S. WALLIS

RECEIVED MARCH 9, 1932
PUBLISHED APRIL 6, 1932

## BETA-SUBSTITUTED FURANS

*Sir:*

Absolute orientation studies of nuclear substituted furans are circumscribed by the paucity of simple *beta*-substituted furans, which are uncommonly difficult of synthesis. 3-Furancarboxylic acid is now accessible by the preferential pyrolytic decarboxylation of 2,4-furandicarboxylic acid. Although the halogen in 3-iodofuran is extremely inert, particularly toward magnesium and sodium, 2,5-dimethyl-3-iodofuran readily forms an organomagnesium iodide. The iodofurans were prepared from the furan-mercurials.

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RECEIVED MARCH 10, 1932
PUBLISHED APRIL 6, 1932

## PREPARATION OF 7,7′-DIMETHYL-8,8′-DIQUINOLYL AND OF 5,5′,7,7′-TETRAMETHYL-8,8′-DIQUINOLYL

*Sir:*

The possibility of optical isomerism in substituted diquinolyls has been suggested by Mascarelli [*Gazz. chim. ital.*, **58**, 627 (1928)]. The preparation of such compounds has been under way at this Laboratory for nearly two years.

7,7′-Dimethyl-8,8′-diquinolyl was made by coupling two molecules of 3-nitro-2-iodotoluene by means of copper powder. The resulting dinitrodimethyldiphenyl was reduced and converted by a Skraup synthesis to 7,7′-dimethyl-8,8′-diquinolyl. It is a white solid, melting at 213–215°. It is insoluble in water, but soluble in dilute acids and in alcohol, benzene and ether.

5,5′,7,7′-Tetramethyl-8,8′-diquinolyl was made by coupling two molecules of 5-nitro-4-iodo-1,3-dimethylbenzene with copper powder. The resulting dinitrotetramethyldiphenyl was reduced and converted by a Skraup synthesis to 5,5′,7,7′-tetramethyl-8,8′-diquinolyl. The substance is a white solid similar in properties to the dimethyldiquinolyl. The preparation of larger quantities of these and other substituted diquinolyls is now under way and attempts are being made to resolve the compounds.

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Henry P. Ward
Mary Grace Waring

Received March 11, 1932
Published April 6, 1932

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## THE STRUCTURE OF ALPHA-PENTAACETYLFRUCTOSE AND ALPHA-CHLOROACETYLFRUCTOSE

*Sir:*

In 1915 Hudson and Brauns [This Journal, **37**, 1283, 2736 (1915)] described two crystalline pentaacetates of fructose which they believed to constitute an $\alpha,\beta$-stereoisomeric pair.

In 1920 Brauns [*ibid.*, **42**, 1846 (1920)] prepared from tetraacetylfructose two chloro compounds which he assumed to be $\alpha$- and $\beta$-stereoisomers. Subsequently his designation of the two forms was reversed at the suggestion of Dr. Hudson and now the substance showing $[\alpha]_D$ $-161°$ in chloroform solution is known as $\beta$-chloroacetylfructose whereas the one with $[\alpha]_D$ $+45°$ is assigned the $\alpha$-configuration.

Using the rotations of these chloro compounds to determine the applicability of the principle of optical superposition to derivatives of the ketone sugars, Dr. Hudson [*ibid.*, **46**, 477 (1924)] calculated the rotations of the fructose pentaacetates. From his results he concluded that the compound with the positive rotation is probably not the true $\alpha$-form. This conclusion is supported by the differences in properties of the two known pentaace-

tates. However, the extreme dissimilarity of the two chloroacetylfructoses suggests that they, too, may not constitute an $\alpha,\beta$-pair. Dr. Brauns has remarked on their great difference in stability.

We now have experimental evidence that the so-called "$\alpha$-chloroacetylfructose" and the "$\alpha$-pentaacetylfructose" differ *structurally* from their isomer in that they are derivatives of the open-chain fructose and contain a free ketone group. The strongest evidence for the presence of a ketone group in "$\alpha$-pentaacetylfructose" is its catalytic reduction to the alcohol. On account of the new asymmetric carbon atom formed during the reduction, sorbitol and mannitol derivatives should be obtained. After acetylation two compounds were isolated and identified as hexaacetylmannitol and hexaacetylsorbitol with melting points 121 and 97°, respectively.

Under the same conditions of reduction the "$\alpha$-chloroacetylfructose" took up hydrogen and there resulted a substance which, like the starting material, contained a very stable chlorine atom.

The chlorine atom in "$\alpha$-chloroacetylfructose" could not be replaced by heating the substance in acetic anhydride solution with silver acetate. This behavior suggests the presence of a firmly bound, primary chlorine atom.

For these reasons we conclude that the "$\alpha$-chloroacetylfructose" represents a derivative of the open-chain fructose with a chlorine atom at carbon atom 6.

The details of this investigation will be published within a short time.

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EUGENE PACSU
FRANK V. RICH

RECEIVED MARCH 12, 1932
PUBLISHED APRIL 6, 1932

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## THE CONSTANT *a* IN THE DEBYE-HÜCKEL LIMITING EQUATION

*Sir:*

In THIS JOURNAL for February, 1932 (p. 831), Professor Hall discusses the numerical value of the constant $a$ in the Debye–Hückel limiting equation: $-\log f = aC^{1/2}$, and refers to a publication ("Conductivity of Solutions," 1930) in which I pointed out that attempts to determine $a$ experimentally have always led to values nearer to 0.4 than to the theoretical value 0.5.

In the same place I remarked that further data on the point are needed, and that conductivity measurements probably provide the most accurate way of obtaining them. Since then, Mr. Banks in this Laboratory has made conductivity measurements on mandelic acid at 25° which agree, after applying Onsager's correction for the mobility changes, with the theoretical value of $a$. We had intended to study further weak acids, but abandoned this plan when MacInnes and Shedlovsky [THIS JOURNAL, **53,**

2419 (1931)] announced that their new conductivity measurements on acetic acid were in complete agreement with the Debye–Hückel value $a = 0.505$.

I think that these two independent investigations provide the best possible verification of the theoretical formula, and it is interesting to find that Hall's calculations on hydrochloric acid are also in agreement with them. Incidentally, further support, if that were needed, for the theoretical value is afforded by the most recent solubility measurements [La Mer and Goldman, THIS JOURNAL, **51**, 2632 (1929), on thallous iodate; unpublished measurements in this Laboratory on barium iodate]. I am glad, therefore, to express my agreement with Professor Hall's conclusions, and have already taken an opportunity of replacing the older, misleading figures in the book to which he refers.

C. W. DAVIES

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RECEIVED MARCH 22, 1932
PUBLISHED APRIL 6, 1932

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## NEW BOOKS

**Svante Arrhenius.** By ERNST H. RIESENFELD, Professor at the University of Berlin. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1931. 110 pp. Illustrated. 16 × 23.5 cm. Price, unbound, M. 7; bound, M. 8.50.

This is a biographical sketch giving a readable and clear delineation of Svante Arrhenius and his important place in contemporaneous science for a third of a century, accompanied by a bibliography. The author shows a thorough understanding of men and events as well as of the important part played by the dissociation theory in the decade and a half prior to 1900, when the infant science of physical chemistry was going through its growing pains. Students of the history or philosophy of science will gain an insight from this book into the obstacles that ideas in advance of the times frequently and probably quite generally have to overcome before being accepted.

"There are not many scientists who have shaken so deeply the foundations of their science and pointed the way for its future development so far in advance as Svante Arrhenius, the creator of the doctrine of electrolytic dissociation," the author very truly states in the opening paragraph.

The tardy recognition of Arrhenius by scientific men in his own country is regrettable but not unusual, and perhaps we may say even according to the Scriptures. The reader, at least the American reader, is somewhat puzzled by several references to the work of Arrhenius' enemies in retarding his scientific advancement because no reasons are apparent why he should have had enemies, or at least active ones, particularly as the picture painted of him by the author is that of a genial, modest personality without conceit.

That Arrhenius should have produced in 1906 a scientific best seller, "Das Werden der Welten," which was translated into seven languages, thus long antedating in a way Eddington and Jeans, will come as a surprise to many. He had an appreciation of the human side of knowledge, for in one letter he expresses his disapproval of piling data into big books that are seldom opened; and the present writer remembers that Arrhenius, when at the St. Louis World's Fair in 1904, expressed the comforting doctrine that as much knowledge may be gained from amicable discussions with one's friends over refreshments as from books. His ruddy complexion and somewhat rotund appearance fitted in with this remark which, however, should not be interpreted too literally, for what he had in mind was the stimulating effect of personal contacts. His students quickly felt how much he himself had to give in this way.

Besides the dissociation theory and its consequences—that great flash of the creative imagination of his youth which probably will remain his greatest monument—his other important contributions resulted from applying his comprehensive knowledge, coupled with exceptionally clear mathematical insight, to other fields of science such as cosmic physics and even the chemistry of immunity.

Gifted with fine perceptions in human affairs as well as in science, he held high ideals for human conduct and for civilization. The World War came as a profound shock to him; nevertheless, he kept his balance and his letters at that period show moderation, insight and as usual a point of view far in advance of the times. During the war his position in science and as a neutral enabled him to help many scientists of the warring nations, and in the years immediately following he was instrumental in reëstablishing friendly relations among men of science of all nations.

As a biography some readers may feel that the book is all too brief.

EDWARD MALLINCKRODT, JR.

**Mass, Zahl und Gewicht in der Chemie der Vergangenheit. Ein Kapitel aus der Vorgeschichte des sogenannten quantitativen Zeitalters der Chemie. (Measure, Number and Weight in the Chemistry of the Past. A Chapter from the Early History of the So-Called Quantitative Period of Chemistry.)** By Prof., Dr., Dr.-Ing. e. h., PAUL WALDEN, Rostock. Verlag von Ferdinand Enke, Stuttgart, Germany, 1931. 106 pp. 16.5 × 25 cm. Price, RM. 10.

This is a most interesting essay in historical chemistry. The first chapters trace the development of the units of weight and of volume from 3000 B.C. to 1775 A.D. The reader will be astonished at the longevity of many of the units, for instance, the old Babylonian Mine (491.25 grams) and the old Egyptian Woten (454.79 grams) or water equivalent of the unit of volume, the Hin, in use as early as 3000 B.C., which persisted through Greek, Roman and Medieval equivalents to appear as our Troy and avoirdupois pounds of today (492.17 and 453 grams, respectively).

In the next chapters there is traced the history of the law of the conservation of matter (500 B.C. to 1789 A.D.). Here the author makes it clear that as a matter of fact Lavoisier in referring to this matter only gave expression to what he took to be a well-nigh universally accepted principle and that later biographers are responsible for crediting him incorrectly with its *discovery*.

Similarly in the following chapter the author shows that contrary to prevailing ideas the increase in weight experienced by metals during calcination had been demonstrated repeatedly between 1300 and 1775 A.D.—that is, previous to Lavoisier—and that the correct explanation of this phenomenon had more than once been given.

Two chapters are then devoted to the history of the discovery and preparation of mineral acids from the time of their discovery (1100 A.D.) until the introduction of modern methods (1800 A.D.), particularly as regards the relative weights of ingredients used.

A final chapter is devoted to the beginnings of quantitative chemical analysis—with special reference to the surprisingly accurate determinations of Wenzel (1777).

This book deals in an interesting and illuminating fashion with matters of the greatest importance in the history of chemistry.

ARTHUR B. LAMB

**Potentiometric Titrations.** A Theoretical and Practical Treatise. By Dr. I. M. KOLTHOFF, Professor of Analytical Chemistry, University of Minnesota, and N. HOWELL FURMAN, Ph.D., Associate Professor of Chemistry, Princeton University. Second edition, extensively revised. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1931. xiv + 482 pp. 74 figs. 15.5 × 23.5 cm. Price, $6.00.

So much work has been done in this field since the appearance of this book in 1926 that the second edition, which is 40% larger, was greatly needed. Besides having been brought up to date, one improvement is particularly noticeable. The first three chapters of the old book dealing with the principles of volumetric reactions have been omitted because they are available elsewhere and in their place is a general chapter devoted to the theory of potentiometric titrations. In Part II, the length of which has been more than doubled, descriptions of new apparatus and technique have been added, among which may be mentioned the differential method, Cavanagh's method and thermionic devices. Part III, devoted to practical applications, has been increased by 25%, an indication of much progress in this field. Among the additions are many methods using ceric sulfate as an oxidizing agent and chromous salts as reducing agents. A complete description is given of existing methods of potentiometric analysis, together with a comprehensive bibliography.

There is no other book which thoroughly covers this field. It is in-

dispensable to the up-to-date analytical chemist as well as to one who is more interested in the theoretical aspect of this subject.

HOBART H. WILLARD

**Practical Physical Chemistry.** By Professor ALEXANDER FINDLAY. Fifth edition. Longmans, Green and Co., New York, 1931. xii + 312 pp., illustrated. 14 × 21.5 cm. Price, $2.25.

A number of new experiments have been introduced into this fifth edition dealing, *inter alia*, with gaseous dissociation, vapor pressure of liquids, viscosity of highly viscous liquids, potentiometric measurements, the use of indicators for the determination of hydrogen-ion concentration, the vapor pressure of salt hydrates and the freezing point of binary systems. Some material has been omitted in order to make space for these new experiments. The concept of activity is used in the treatment of strong electrolytes and an experiment is included dealing with the effect of a salt on the activity of hydrogen ion. As in previous editions experiments are preceded by a brief theoretical discussion which together with many diagrams and graphs should make the student largely independent of reference books. The variety of experimental methods and large number of systems suggested for study in certain experiments give this manual a wide range of usefulness.

HENRY E. BENT

**List of Periodicals Abstracted by Chemical Abstracts with Key to Library Files.** Edited by E. J. CRANE. Revised edition. *Chemical Abstracts*, The Ohio State University, Columbus, Ohio. 142 pp. Price, 50 cents.

No chemist has direct access to all of the many periodicals of chemical interest and many have very poor library facilities. This circumstance is no longer the serious handicap in chemical work that it once presented because the List of Periodicals with its key to library files, coupled with the fact that many libraries now maintain a photoprint or a lending service, makes it possible for any chemist anywhere quickly to get almost any chemical paper at a reasonable cost. The list serves to bridge the gap between abstracts and full papers.

Key numbers are given for 250 libraries scattered throughout the United States, Canada and Hawaii.

In addition to the library information the List gives for each periodical the full title, the official abbreviation, the frequency of appearance, the 1931 volume number (the first if there is more than one per year), the first number of that volume if other than 1, the number of volumes per year, the price and the name and address of the publisher.

Besides entries for 1996 live periodicals, the new List contains 1104

entries which either tell of discontinued periodicals or take the form of cross references from former names, from transliterated names (mostly Japanese and Russian) or from the names of institutions sponsoring periodicals.

The List is published every five years. It has grown from a 60-page booklet in 1922 to one of 142 pages of 2-column fine print. Because of its completeness it has come to be used to a considerable extent as a check list in the building and maintenance of scientific libraries and also in chemical literature courses in the universities. Even though the latest List was published as a part of the regular November 20th number (1931) of *Chemical Abstracts*, the demand for extra copies in separate form, anticipated from experience with earlier lists, has been met by the provision of a supply of reprints. Copies of these can be obtained by writing to the office of *Chemical Abstracts*.

CHARLES L. PARSONS

**Oxydations et Réductions. (Oxidation and Reduction.)** By RENÉ WURMSER. Les Presses Universitaires de France, Paris, France, 1930. xix + 381 pp. Price, fr. 95.

This is one of a series of monographs dealing with problems in biology and this fact is perhaps a better indication of the nature of the book than its title. The author considers the application of thermodynamics to a variety of biochemical processes in which oxidation or reduction is involved. These include photosynthesis, chemosynthesis, the specific dynamic action, the chemical changes involved in muscular action and a great variety of enzymatic processes. The treatment of the energetics of oxidation and reduction employs the terminology of Lewis and Randall and gives a precise and clear account of the application of free energy equations to one phase of organic chemistry. The only criticism that the reviewer would make of this very excellent feature of the book is the failure to discuss the probable uncertainties in the values of the free energy of a reaction calculated by means of the third law. For example, the value of $\Delta F$ for the formation of carbon dioxide and hydrogen from glucose and water is given as $-6277$ cal., which is arrived at by taking the difference between $\Delta H = 145{,}220$ and $T\Delta S$ of 151,497, and no hint is given of the fact that the uncertainties in the present values make $\Delta F$ uncertain by at least $\pm 1000$ cal. The last half of the book deals with the measurement of oxidation–reduction potentials and their application to biological problems. All the important work in this field through 1929 seems to have been covered, and the results are given in considerable detail but without much attempt at a critical evaluation of their significance. Here, as elsewhere in the book, the handling of the physico-chemical aspects of the subject is superior to the treatment of the problems of interest to the

organic chemist. It is particularly unfortunate that a completely erroneous structural formula for hemin should be given.

The book will be of great interest and value to those who are concerned with the energetics of biochemical reactions and indispensable to the specialist in the subject of oxidation and reduction. The sections dealing with fields in which the author himself has been an investigator (for example, photosynthesis) are particularly interesting.

JAMES B. CONANT

**Laboratoriumsbuch für die kolorimetrische Wasseruntersuchung. (Laboratory Manual for Colorimetric Water Analysis.)** By PAUL MARTINY. Druck und Verlag von Wilhelm Knapp, Halle (Saale), Germany, 1931. vii + 73 pp. 26 figs. 16 × 23 cm. Price, unbound, RM. 5.40; bound, RM. 6.80.

This little book is Volume 28 of "Laboratory Manuals for Chemical and Allied Industries." It is divided into two parts of about equal length. Part I deals with general directions for colorimetric analysis and gives brief descriptions (with illustrations) of the following colorimeters: Wolf, Donnan, Duboscq, Bürker, Bjerrum–Arrhenius (double-wedge), Martiny (compensation), Krüss (polarization), Hillige (comparator), Folin–Wulff, Pulfrich (photometer) and Olzewski–Rosenmüller (photometer).

In Part II procedures are given for the following determinations in the order listed: aluminum, ammonium, lead, copper, bromide, chlorine, chromate, iron, iodide, potassium, calcium, silica, magnesium, manganese, sodium, phenol, phosphate, protein nitrogen, thiocyanate, nitrate, nitrite, sulfate, hydrogen sulfide, zinc, caramel, turbidity and hydrogen ion.

JOHN H. YOE

**Über die Fehlerquellen bei der mikroanalytischen Bestimmung des Kohlen- und Wasserstoffes nach der Methode von Fritz Pregl. (Sources of Error in the Microanalytical Determination of Carbon and Hydrogen by the Methods of Fritz Pregl.)** By Dr.-Ing. MAX BOËTIUS, Lecturer at the Technical High School of Dresden. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1931. 113 pp. 15.5 × 22.5 cm. Price, RM. 7.

The well-known micro combustion method of Pregl is admirably simple in principle and possesses a high degree of reliability in the hands of the experienced worker. But for special reasons it is more susceptible to errors than other microanalytical methods, and occasionally failures are encountered even when Pregl's directions are strictly followed.

Basing his experiments on Pregl's work, Dr. Boëtius by a careful and systematic study of these disturbing influences has endeavored to disclose and eliminate certain errors which in his opinion were not fully recognized or sufficiently emphasized by Pregl. This program has naturally involved a laborious reëxamination of the experimental details of the method.

The number of new facts contributed by the investigation is comparatively small. Nevertheless, there are many points which merit the interest of the microanalyst. Special mention may be made of the paragraphs dealing with the errors due to the employment of lead peroxide (retention of water), and with the factors which influence the constancy of weight of the absorption tubes (temperature, humidity, nature of the absorbing material, condition of the rubber connections). Certain suggestions regarding apparatus and technique may prove to be of practical value.

Apart from the experimental contributions to the problem, the book serves a didactic purpose, being supplementary to the monograph of Pregl. It is particularly valuable to the novice since he will find there accurate quantitative statements, in the form of experimental records, indicating to what extent each individual source of error may influence the result. In addition, the detailed description of the experiments may convey to him some conception of the means whereby the various errors may be detected and eliminated. Also, papers previously published on the subject are discussed in connection with the author's own findings. The broad yet detailed treatment may well be due both to the nature of the topic and to the example set by Pregl's excellent monograph.

O. WINTERSTEINER

**Jahrbuch der organischen Chemie. (Yearbook of Organic Chemistry.)** By Professor Dr. JULIUS SCHMIDT, Stuttgart. Vol. XVII, 1930. Verlagsbuchhandlung von Franz Deuticke, Wien, Austria, 1931. xvi + 300 pp. 17 × 25.5 cm. Price, M. 30; bound, M. 33.

By the publication of two volumes in both 1930 and 1931 the "Yearbook of Organic Chemistry" has been brought completely up to date, an achievement on which both the editor and the publisher are to be congratulated. In the present edition, as in its predecessors, the reviews are entirely objective, the reviewer accepting, almost invariably without discussion or criticism, the interpretations given in the papers under review. The organization of the material likewise remains the same as heretofore but the prevailing interest in natural products is clearly reflected in the steadily increasing space devoted to this subject.

E. P. KOHLER

# BOOKS RECEIVED

February 15, 1932–March 15, 1932

K. BERNHAUER. "Die Oxydativen Gärungen." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 196 pp. RM. 16.80; bound, RM. 18.

KARL KELCHNER DARROW. "Electrical Phenomena in Gases." The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Md. 492 pp. $8.00.

ALEXANDER FINDLAY. "Chemistry in the Service of Man." Fourth edition. Longmans, Green and Co., 55 Fifth Ave., New York. 355 pp. $2.50.

ERNST GALLE. "Hydrierung der Kohlen, Teere und Mineröle." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 111 pp. RM. 9; bound, RM. 10.

J. SAMUEL GUY AND AUGUSTA SKEEN. "A Course in Quantitative Analysis." Ginn and Company, 15 Ashburton Place, Boston, Mass. 242 pp. $2.20.

FELIX HAUROWITZ. "Fortschritte der Biochemie. II. Teil (1924–1931)." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 152 pp. RM. 11; bound, RM. 12.

F. STANLEY KIPPING AND F. BARRY KIPPING. "Perkin and Kipping's Organic Chemistry." New edition. J. B. Lippincott Company, 227 South Sixth St., Philadelphia, Pa. 642 pp. $3.50.

RAPH. ED. LIESEGANG, Editor. "Kolloidchemische Technologie." Second, revised edition. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 1085 pp. RM. 68; bound, RM. 72.

F. A. LINDEMANN. "The Physical Significance of the Quantum Theory." Oxford University Press, 114 Fifth Ave., New York. 148 pp. $2.50.

W. SCHRÖTER. "Das Rhenium." Verlag von Ferdinand Enke, Stuttgart, Germany. 59 pp. RM. 5.50.

WILLIAM R. SMYTHE AND WALTER C. MICHELS. "Advanced Electrical Measurements." D. Van Nostrand Company, Inc., 250 Fourth Ave., New York. 240 pp. $3.00.

SELMAN A. WAKSMAN. "Principles of Soil Microbiology." Second edition. The Williams and Wilkins Company, Mt. Royal and Guilford Aves., Baltimore, Md. 894 pp. $10.00.

CLARENCE J. WEST AND D. D. BEROLZHEIMER, Compilers. "Bibliography of Bibliographies on Chemistry and Chemical Technology." Second Supplement, 1929–1931. Bulletin 86 of the National Research Council. Published by the National Research Council of The National Academy of Sciences, 2101 Constitution Ave., Washington, D. C. 150 pp. $1.50.

ANDREW L. WINTON AND KATE BARBER WINTON. "The Structure and Composition of Foods." Vol. I. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 710 pp. $8.50.

"The Life and Works of Professor William Henry Perkin." Published by the Chemical Society, Burlington House, London, W 1, England. 138 pp. 3/6; postage, 3 d.